Development of Functional Adsorbent from Natural Biosorbent "Chitosan" by Radiation Induced Grafting of MAETC for the Removal of Arsenic (V)

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ABSTRACT

High energy gamma radiation has been used to graft [2-(methacryloyloxyethyl) trimethylammonium chloride (MAETC) onto chitosan by radiation grafting method. Grafting yield was found to increase with the increase in radiation dose and monomer concentration. Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the grafted polymer and their morphological structure was analyzed by Scanning Electron Microscope (SEM). As(V) ions uptake capacity of the adsorbent was evaluated in different pH, contact time, temperature, adsorbent dose, and different arsenate ion concentration. The adsorption data was fitted well in the Langmuir model and various static parameters were calculated. It is stated that this chitosan-g-MAETC could be regenerated efficiently (>90 %) and used repeatedly.

KEYWORDS: *Chitosan, MAETC, Grafting, Adsorption, Arsenic (V), Irradiation.*

1. INTRODUCTION

The presence of arsenic in groundwater, eventually in drinking water, has been recognized as a serious community health problem due to its high toxic nature and therefore, its removal is highly essential. Arsenic enters the ecological system via a combination of natural process and anthropogenic activities. Exposure to arsenic through drinking water sourced from groundwater cause a serious health hazards like melanosis, leucomelanosis, keratosis and skin cancer etc[1]. Arsenic has been used in medicine, agriculture, livestock, electronics, industry and metallurgy[2,3]. Generally arsenic occurs in the environment in many oxidation

states such as -3, 0, +3 and +5. It exists in two forms i.e. inorganic and organic arsenic. Inorganic arsenic is generally found as trivalent arsenite or pentavalent arsenate form in aqueous solution. In surface water under oxidizing conditions, As(V) predominates while As(III) becomes stable in anaerobic water under reducing conditions. In surface water under oxidizing conditions, As (V) predominates while As(III) becomes stable in anaerobic water under reduced conditions. As high as, the WHO provisional guideline of 10 µg/L of arsenic in drinking water is now recognized as a worldwide problem in many countries, especially in the Southeast Asia, including India, Bangladesh and China[4].

Developing technologies to remove arsenic from aqueous system has become a major interest of research in recent years. The most applied techniques for arsenic removal from water are chemical precipitation/coagulation, adsorption, ion exchange and membrane filtration[5,6] etc. However the effectiveness of these methods for removing arsenic at low concentrations is less, time taking and could be relatively expensive [7,8]. Adsorption is considered as the best for the treatment of water and wastewater in terms of convenience, profitability, design and significant arsenic removal efficiency. Besides, it is most suitable due to availability of a wide range of adsorbents.

A number of natural polymers that exist in nature are - cellulose, gelatin, alginate, dextran and chitin/chitosan etc. Chitosan finds variety of applications in many industries due to its unique properties such as bio-compatibility, bio-degradability and non toxicity. Chitosan has been widely applied in water treatment due to the presence of a reactive amino group at position 2, and a hydroxyl group at position 3. Chitosan also forms chelates[9] with large number of metals. However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values and gives some major difficulties in sorption process, i.e. quite low mechanical properties and heat resistance, solubility in acidic media, high swelling ratio and limited sorption capacity for few metal ions. In order to enhance the adsorptive property of chitosan, it was modified through grafting. The main grafting techniques involve either chemicals[10] or by the use radiation[11]. We have used the radiation induced grafting method to modify the natural polymer "chitosan" because it is easy, efficient and more advantages as compared to chemical method. The advantages of this method are rapidly creating radicals in the trunk polymer by irradiation without the use of any chemical reagents and causing no significant changes in the properties of the base polymer[12,13]. Many scientists have reported different adsorbents namely, chitosan–silica composite, iron oxide coated sand, iron nano-particle resin and polymeric hybrid sorbent[14-24] for arsenic removal from the aqueous solutions, but only a few work has been reported on grafted the polymers on natural polysaccharides. Therefore, a keen attention and serious effort is required to generate more efficient and low cost and biodegradable polymer to remove the toxic arsenic ions from water. Hence in the present study, we have synthesized a novel non-toxic, biodegradable and efficient adsorbent by grafting of a cationic monomer (MAETC) onto natural biopolymer, chitosan using gamma radiation

for the removal of arsenic. By introducing a quaternaryay group present in MAETC onto chitosan, it could be possible to improve its stability and adsorption capacity towards the arsenate ions at low pH.

EXPERIMENTAL

Materials

Chitosan degree of deacetylation not less than 85% medium molecular weight was purchased from Aldrich.

2-Methacryloyloxyethyltrimethylammoniumchloride (MAETC), mol wt. = 207.7, purity > 99% in the form of a 75% aqueous solution from Fluka. EGDMA (Ethylene glycol dimethylacrylate) and sodium arsenate were obtained from M/s SD Fine chemicals, Mumbai and were used as received. All other chemicals used were of AR grade. Double distilled water was used for preparing all solutions and for water uptake studies.
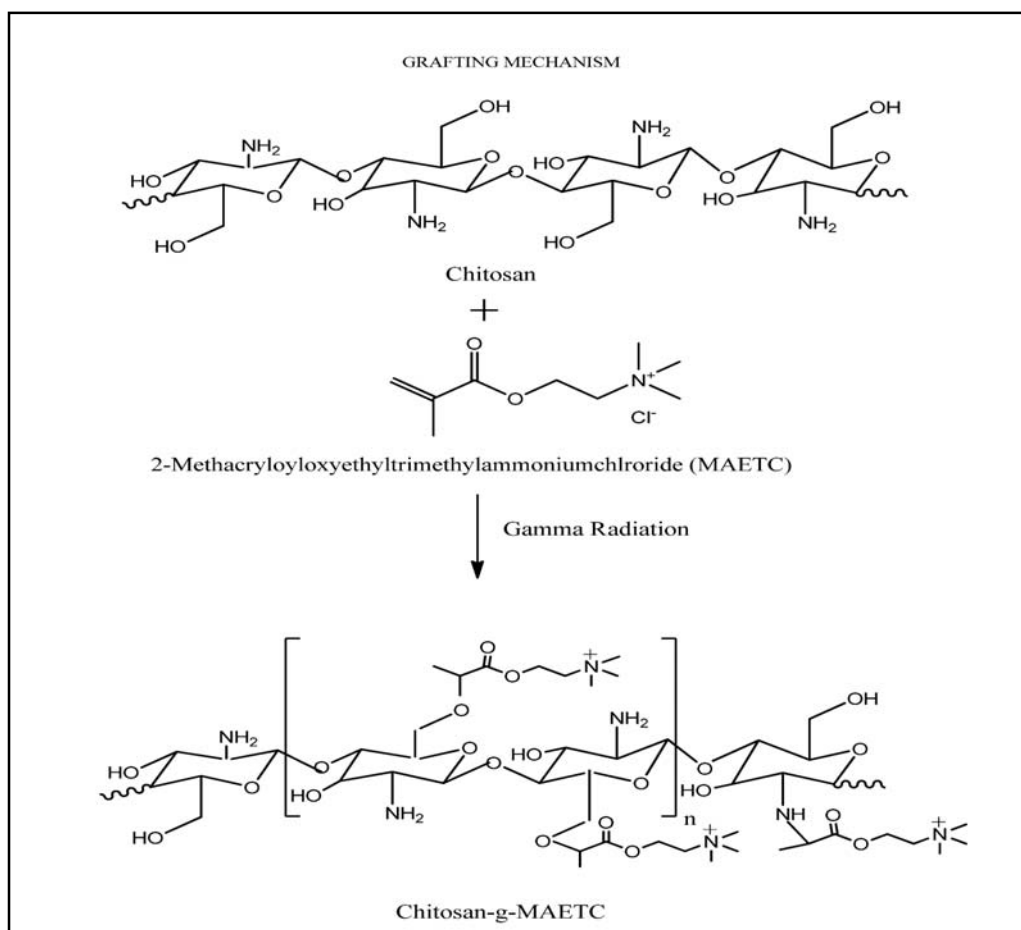
Radiation induced grafting of MAETC onto chitosan

Fixed quantity of chitosan (5%) and MAETC monomer having different concentrations were mixed and EGDMA

Scheme 1. Grafting of MAETC onto bio-polymer chitosan

(Ethyleneglycoldimethylacrylate) was added in it. The mixture was thoroughly stirred and poured into clean glass vials (inner diameter 2 cm and length 7–8 cm). Polymerization was carried out by irradiating the sealed samples with ambient conditions at room temperature (29±1°C) with gamma rays from a ^{60}Co g-source at a dose rate of 5 kGy/h, as determined by Fricke dosimetry. After irradiation the glass vials were carefully broken and the grafted polymer in cylindrical form was cut into 0.5–1.0 mm thick disks with a sharp knife and washed with double distilled water to remove unreacted monomer and other impurities.The grafted sample was dried in an oven at 40°C to get constant weight. The dried samples were stored for further experimental use. The mechanism of grafting of MAETC onto chitosan is shown in Scheme 1.

The grafting yield was determined gravimetrically using the relation as follows,

$$\text{Grafting yield (\%)} = \frac{Wg - Wo}{Wo} \tag{1}$$

Where W_o and W_g are the weight of raw and grafted chitosan respectively.

Water uptake study

Chitosan grafted MAETC with different grafting yields were immersed in water at 25±1°C until equilibrium was reached. The excess water on the surfaces of wet samples was wiped out with tissue paper and the samples were weighed. The water uptake capacities of the samples were estimated using the following relation:

$$\text{\% Water uptake} = \frac{Ws - Wd}{Wd} \times 100 \tag{2}$$

Where W_s is the weight of swelled weight and W_d is the dried weight(g).

FTIR spectroscopy

Fourier transformed infrared spectroscopy (FTIR) measurements were performed using FTIR spectrophotometer (Thermo Nicolet, Avatar 380) in the range from 4000-400cm^{-1} with a resolution of 4 cm^{-1} and averaged over 32 scans.

SEM

Scanning Electron Microscope (SEM) using JEOL (Model JSM – 6390LV) equipment investigated the surface morphology of the chitosan and grafted chitosan.

Batch adsorption experiments

Simple preliminary batch experiments were carried out to examine the adsorptive performance of chitosan-g-MAETC towards As (V). For stock solution of As (V) (1000 ppm), 0.416 g of $Na_2HAsO_4.7H_2O$ was dissolved in 100 ml double distilled water and then working solutions were prepared by dilution to get the appropriate concentrations. Then 30 ml aliquots of (20 - 100 ppm) were prepared and shaken with 0.1 g of adsorbent using wrist action shaker for a definite period of time and adsorption of arsenic was analyzed. As role of pH of the solution plays an important role on the adsorption of noxious As (V) using chitosan-g-MAETC; the influential parameter was well studied and optimized using the equilibrium adsorption tests at different solution pH in the range of 2-10 using 0.1M NaOH and HCl solutions. The initial As (V) concentration and the optimized adsorbent dose were 60 mg/L and 0.1 g respectively. All the experiments were carried out between 2.5-3 pH at room temperature (25±2°C) to reach the equilibrium. After shaking, the supernatant was centrifuged for 5 min and the residual concentration of As (V) was determined by molybdenum blue method[25] and absorbance of blue colored solution was recorded at 750 nm spectro-photometrically (Varian, Cary 60 model).The same adsorption experiments were carried out using ungrafted chitosan. The adsorbed amount of As (V) was calculated by the following mass balance equation:

$$\text{Adsorbed amount (mg/g)} = \frac{(Co - Ce) \times V}{M} \tag{3}$$

$$\text{Sorption degree} = [(C_o - C_e) / C_o] \times 100 \tag{4}$$

where C_o and C_e are initial and equilibrium concentration (ppm or mg/L) of arsenic solution respectively. V is the volume of the solution and M is the weight of grafted chitosan.

Equilibrium isotherms

Equilibrium isotherms were studied at ambient temperature (25±2°C) by the addition of 0.1 g of adsorbent with 30 ml arsenic solution of different concentrations. These suspensions were shaken for 60 min under optimized pH conditions (2.5-3) and these data were applied to Langmuir and Freundlich isotherms.

Adsorption kinetics

For monitoring the progress of the adsorption process, adsorption experiments were run under the optimized conditions, i.e. 0.1g of chitosan-g-MAETC was shaken with 30 ml solution of 60 mg/L of As (V) for 60 min under optimum pH condition (2.5 -3) at room temperature (25) and the amount of adsorbed As (V) was determined in each set at different time intervals (ie.5 min) spectrophotometrically.

Desorption studies

Desorption studies indicate the nature of adsorption and recovery of arsenic from contaminated water and the sorbent. After the sorption experiments, the sorbent was separated by filtration and washed with double distilled water. For the desorption, grafted adsorbent loaded with arsenic was shaken with 30 ml of different concentrations of NaOH solution (0.01- 0.3M) and the amount of arsenic
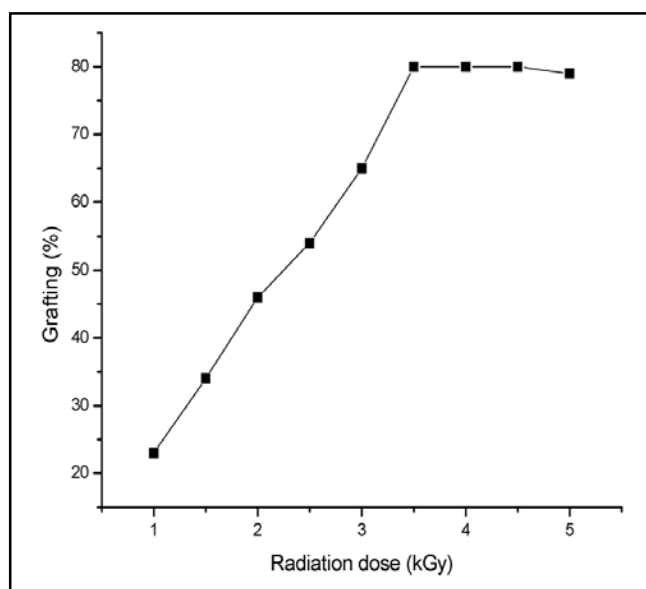

Fig. 1. Effect of radiation dose on grafting

desorbed at different time intervals (30 min, 60 min and 120 min) was determined by molybdenum blue method spectrophotometrically.

$$\text{Desorption efficiency} = \frac{\text{Amount of As (V) desorbed}}{\text{Amount of As (V) sorbed}} \quad (5)$$

RESULTS AND DISCUSSION

Effect of irradiation dose

Fig.1. shows the relationship between radiation dose and grafting yield. It was observed that by the exposure of gamma radiation to the grafting mixture from 1kGy to 5 kGy, the percentage of grafting increased from 20% to 80% up to the dose 3.5kGy and then leveled off. Initially with the increase of radiation dose, more number of free radicals generated at the active sites on the trunk polymer which may induce the grafting process and increases the grafting percentage. There was no significant change in the grafting extent at higher radiation doses
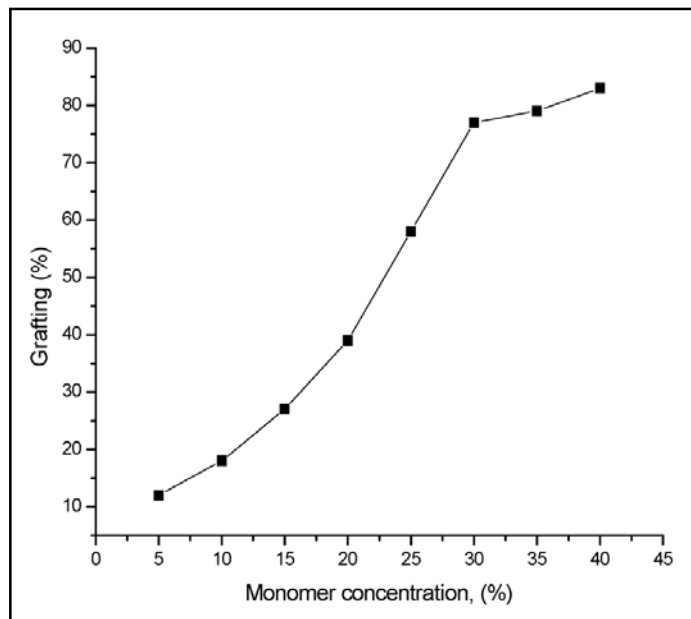
Fig.2. Effect of monomer concentration on grafting

which may be due to either exhaustion of monomer or due to highly viscous nature of the grafting mixture that prevents the monomer diffusion to the propagating grafted chains. The similar results were reported elsewhere[26].

Effect of monomer concentration on grafting

In order to achieve good grafting yield, the effect of monomer concentration is very important. Grafting of MAETC was carried out taking different amounts of monomer keeping the amount of the chitosan constant for fixed radiation dose (3 kGy) under aerated conditions. The results of this study are shown in Fig.2. It was observed that the grafting yield increased almost linearly (10% to 80%) with the increase in monomer concentration in the

range from 10 to 40 % (w/v). Mostly higher grafting yields are expected with higher concentrations of monomer, because the radicals generated on the chitosan backbone would be able to interact with more number of monomer molecules. However at higher monomer concentrations (> 30%), more monomer radicals would be generated in the bulk and homo polymerization will also be equally favored. Therefore, in order to achieve higher grafting levels and low homo polymerization the concentration of monomer was fixed at 30% (w/v).

FTIR spectrum

Infrared spectra of pure chitosan Fig.3a, chitosan-g- MAETC Fig. 3b and As(V) adsorbed chitosan-g- MAETC Fig.3 care illustrated in Fig. 3. The FTIR spectra of
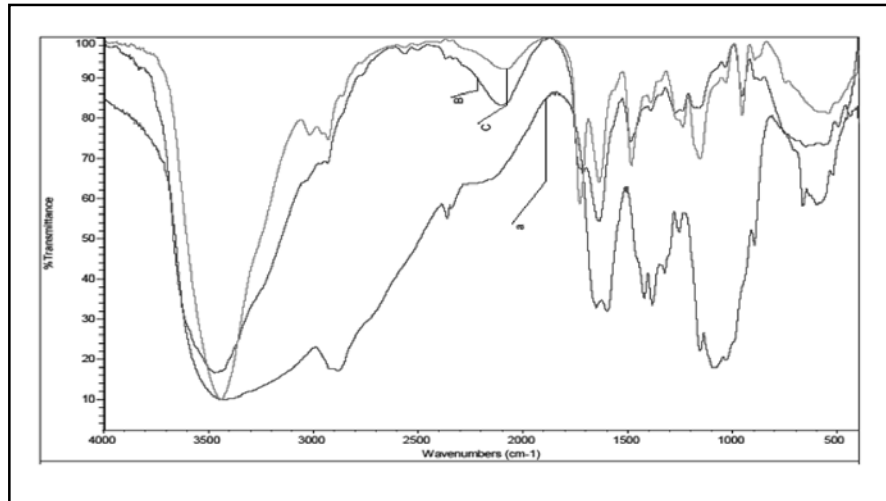
Fig. 3. FTIR spectrum of chitosan (a) chitosan-g-MAETC (b) and As(V) loaded chitosan-g-MAETC (c).

chitosan (a) shows a broad peak at 3500-3200 cm^{-1} due to hydrogen bonded (O-H stretch), 1652 cm^{-1} (N-H deformation), 1383 cm^{-1} (C-N stretch), 1154 cm^{-1} (C-O-C), and 1088 cm^{-1} (C-O stretch). In the chitosan-g- MAETC (b) shows the new signals for functional groups (-N-(CH$_3$)$_3$) at 2700-2250 cm^{-1}(broad band) and 1490cm^{-1}. For ester group signals show at 1712 cm^{-1}(-C=O). In As(V) loaded chitosan-g-MAETC (c) small

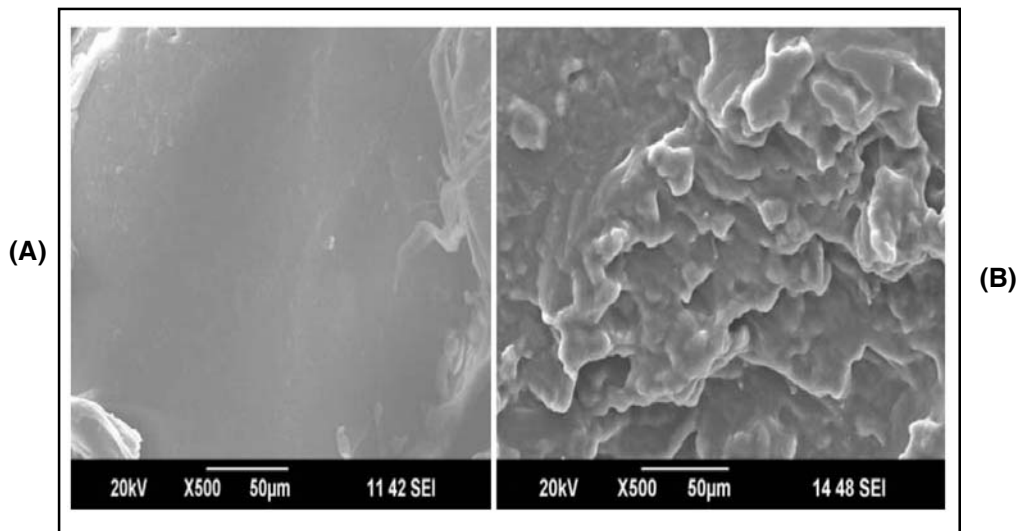
Fig. 4. SEM images of pure chitosan (a) and chitosan-g- MAETC (b)

sharp peaks obtained in the range of 1200 cm^{-1} and 800-458cm^{-1} could be attributed to characteristic vibrations of protonated +NH_3 and +$N(Me)_3$ groups in the grafted polymer interact with $H_2AsO_4^-$ ions (arsenate).

SEM

The surface morphology of chitosan and chitosan-g-MAETC was studied by SEM analysis in the range between 5-50 mm are shown in Fig.4. In Fig. 4(a), no pores could
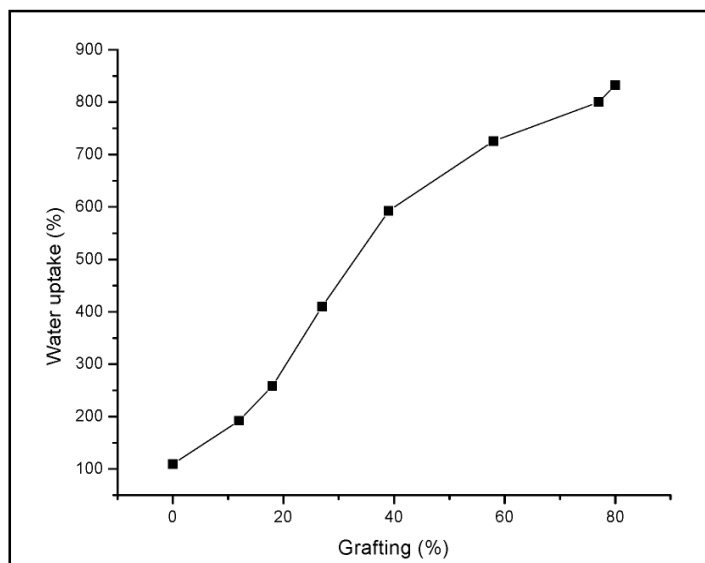

Fig. 5. Relation between grafting degree and Water uptake capacity

be seen before grafting of chitosan, whereas in Fig. 4(b) it shows significantly rougher surface having large number of pores generated by grafting process. The large surface area and uniform porous structure of grafted polymer would definitely enhance the adsorption capacity of the adsorbent towards the arsenate ions.

Water uptake study

The water uptake capacity for different percentage of grafted polymer of MAETC and chitosan was studied to probe this observation. The water absorbency of grafted samples was found to increase linearly with the increase of grafting yield as shown in Fig.5. It was observed that the water uptake capacity was maximum for (chitosan-g-MAETC) having 80% grafting yield. It clearly indicates that the incorporation of ionic monomers onto natural polymers increase the water uptake capacity as reported elsewhere[27].

Factors Affecting Adsorption

Effect of Initial Concentration of As (V) Ions

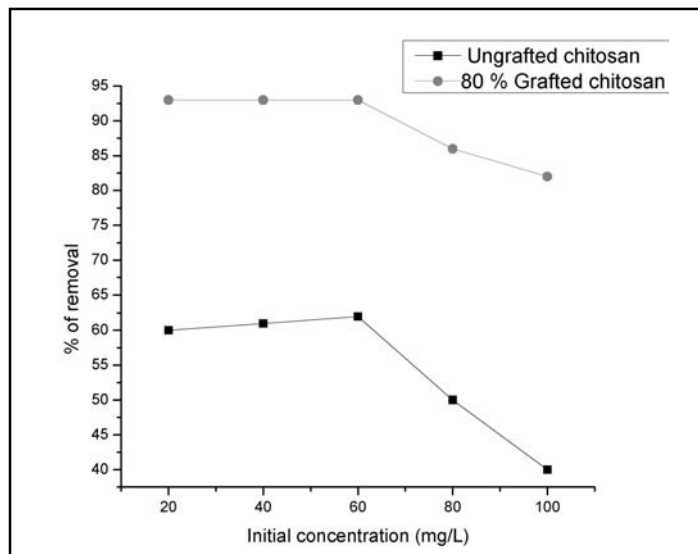The effect of initial concentration on removal of arsenate ions by ungrafted chitosan and

Fig. 6. Effect of initial concentration on adsorption of As (V) ions

chitosan-g-MAETC were studied by performing the adsorption experiments with different As (V) ion concentrations in the range of 20 to 100 mg/L Fig.6 It was found that with the increase of arsenate ion concentration, the percentage removal of As (V) ions increased upto 60 mg/L, after that, the removal efficiency decreased with increasing As(V) concentration which may be due to all As(V) species are not able to come in contact with active sites of the sorbents or exhaustion of binding sites. At low concentrations, most
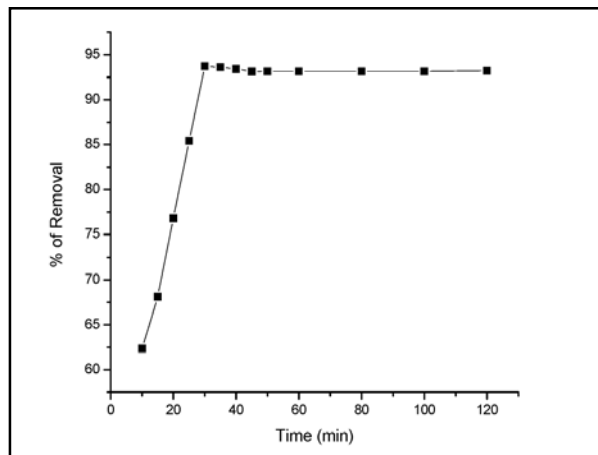

Fig. 7.Effect of contact time on adsorption of As (V)

of the As (V) ions in the solution get enough active sites present on the adsorbent surface, hence get adsorbed. Fig.6. shows the maximum removal percentage of arsenic in ungrafted chitosan is observed 62.3% and in the grafted chitosan it was 94%. From this study, it was evident that the grafting of MAETC onto chitosan plays an important role in arsenic adsorption process.

Effect of Contact Time

It has been observed that removal effciency of As (V) ions increased with an increase in contact time before equilibrium is reached Fig.7. Maximum 93.6 % of the ultimate adsorption capacity occurs within 35 minutes of contact time for As (V) ions. Rapid initial removal rate is possibly due to the availability of sufficient vacant adsorbing sites in presence of higher arsenate ion concentration gradient. Further increase in contact time above 35 min did not increase the uptake due

to deposition of arsenate ions on the available adsorption sites on the adsorbent material. Thus, 35 minutes time was observed to be optimum contact time for the maximum removal of arsenic ions.

Effect of Temperature

Temperature plays an important role on the process of adsorption. Effect of temperature on adsorption of As (V) ions was studied by conducting different sets of experiments at different temperatures in the range from 10 to 40°C. It has been observed that the adsorption of arsenate ions increases from 10 to 25±2°C (room temperature) while beyond 25±2°C, a sudden fall in the adsorption was noticed. At much higher temperature (above 25±2°C) a decrease in adsorption was noticed which may be due to the weakening of binding forces between arsenate ions and active sites on the grafted polymer due to the decreased surface activity.
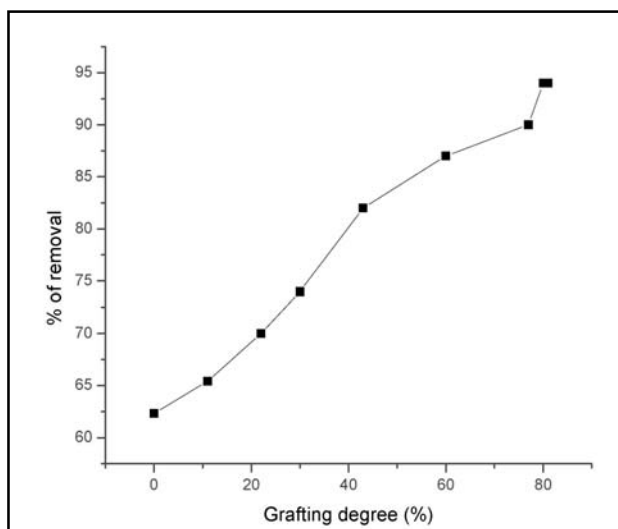

Fig. 8. Effect of grafting degree on adsorption of As (V).

Effect of grafting degree

The effect of removal capacity of As (V) was investigated by using grafted and ungrafted chitosan. For this, 0.1g of ungrafted chitosan and grafted chitosan(with different grafting degree) were shaken with sodium arsenate solution (60 mg/L)for 35 min at room temperature (25±2°C) and the removal percentage of arsenic in each set was determined spectrophotometrically. It was observed that with the increase of grafting degree (from 11% to 80%), the removal percentage of the sorbent increased gradually (from 65% to 94%). Because at higher grafting degree, more number of MAETC groups having the quaternary ammonium groups could interact with arsenate ions, hence the adsorption capacity increased (Fig. 8). But in the case of ungrafted chitosan, due to the absence of MAETC group, it shows only 62.3% removal capacity. From this study, it clearly indicates that grafted chitosan shows greater removal capacity as compared to ungrafted chitosan.

Effect of pH on AS (V) removal

The most important parameter influencing the adsorption capacity is the pH of adsorption medium. Arsenic is sensitive to pH in ground waters (pH 6.5–8.5) under oxidizing and reducing conditions. As it is already reported that under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH "less than 6.9", while at higher pH, $HAsO_4^{2-}$ becomes dominant ($H_3AsO_4^0$ and AsO_4^{3-} may be present in extremely acidic and alkaline conditions,
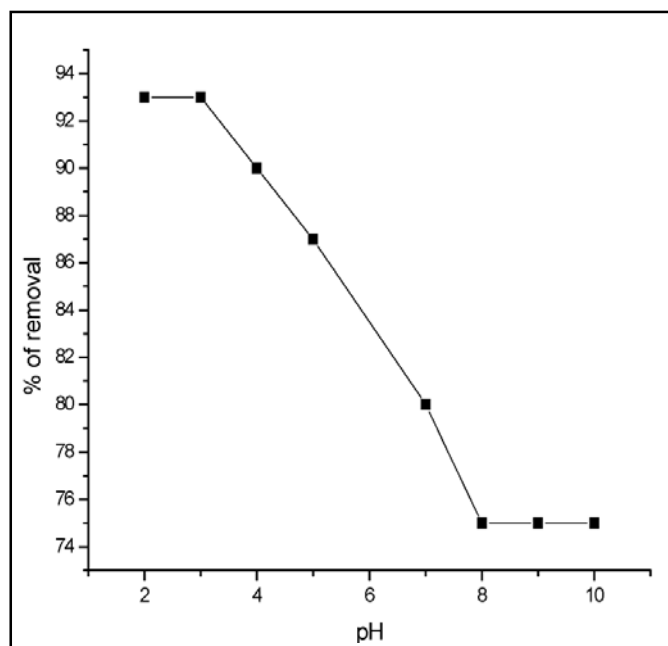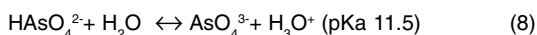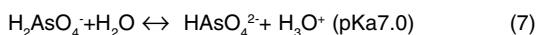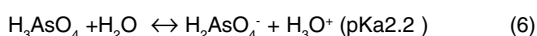

Fig.9. Effect of pH on adsorption of As (V)

respectively). Under reducing conditions at pH less than pH 9.2, the uncharged arsenite species "$H_3AsO_3^0$" predominates[28]. It was also well documented that the functional groups present on the adsorbent surface together with the forms of arsenic species (adsorbate), are strongly pH dependent. The dissociation reaction of arsenic acid (arsenate) is shown below,

$$H_3AsO_4 + H_2O \leftrightarrow H_2AsO_4^- + H_3O^+ \text{ (pKa2.2)} \quad (6)$$

$$H_2AsO_4^- + H_2O \leftrightarrow HAsO_4^{2-} + H_3O^+ \text{ (pKa7.0)} \quad (7)$$

$$HAsO_4^{2-} + H_2O \leftrightarrow AsO_4^{3-} + H_3O^+ \text{ (pKa 11.5)} \quad (8)$$

Arsenate species exist in aqueous phase as H_3AsO_4 at pH less than 2.2, $H_2AsO_4^-$ at pH between 2.2 and 6.98, $HAsO_4^{2-}$ at pH between 6.98 and 11.5 and AsO_4^{3-} at pH above 11.5. Arsenate adsorption on grafted chitosan takes place through ion exchange mechanism involving positively charged amino group and negatively charged arsenate ion depending on the reaction conditions. From Fig.9 it was noticed that the adsorption of As(V) is more favorable at lower pH where the surface of the adsorbent is positively charged. The maximum removal of As(V) was observed between pH 2-3 and above pH 3-10, slow decrease in adsorption was observed. As mentioned earlier, adsorption of As(V) on chitosan-g-MAETC takes place by ionic interaction therefore; above pH 7, where chitosan exists in the neutral form, there is not much interaction between As(V) and grafted chitosan and the observed adsorption is lower. Below pH 2, As(V) exists as H_3AsO_4 and hence cannot interact with protonated grafted chitosan through ion exchange mechanism. Hence, in all the further studies, initial pH of As(V) was adjusted between pH 2.5 to 3.
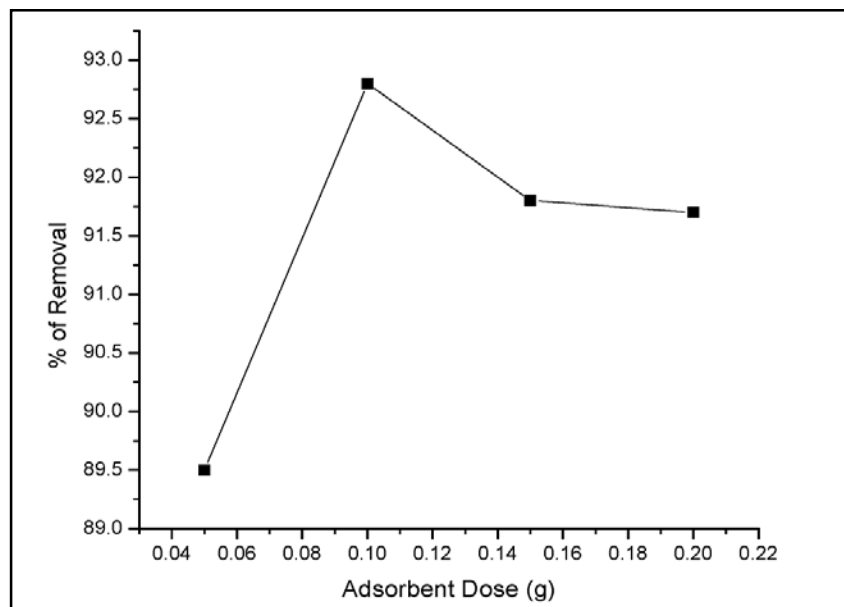

Fig. 10. Effect of adsorbent dose on adsorption of As (V).

Effect of Adsorbent Dosage

The dependence of As (V) sorption on adsorbent dose was studied by varying the amount of adsorbent dose from 0.05 to 0.2 g with fixed volume of adsorbate (30ml) keeping other parameters like pH, contact time, and temperature constant Fig.10. It was observed that the percentage removal of As (V) on adsorbent increased (89.5% to 93%) rapidly with increase in adsorbent dose from 0.05 to 0.1g, which was later followed by slow decrease in removal percentage (91%). This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remain constant even with further addition of the dose of adsorbent. Hence, 0.1g was fixed as optimized adsorbent dose for further adsorption experiments.

Adsorption kinetics

The study of adsorption kinetics is important in describing the adsorption process as it explains how fast the process occurs and also provides information on the factors affecting or controlling the adsorption rate. The experimental data were analyzed and employed pseudo-first-order[29], pseudo-second-order[30] and intra-particle diffusion models.

Pseudo-First-Order kinetics

The kinetics of sorption of arsenate ions from water has been studied using pseudo-first-order (Lagergren equation) as given below

$$dq_t/dt = k_1(q_e - q_t) \tag{9}$$

The integrated modified form of the above equation is written as

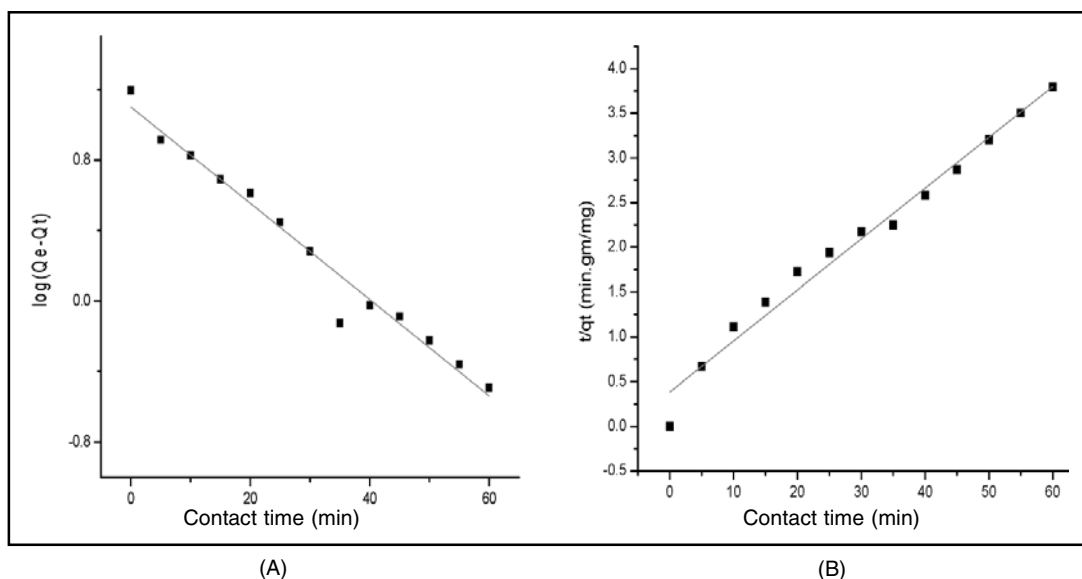$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

Fig. 11. (a) Pseudo first-order kinetics and (b) Pseudo second-order kinetics

where q_e and q_t are the amount of arsenic adsorbed on the adsorbent at equilibrium (mg/g) and time t (min) respectively. k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}). The adsorption rate constant was determined from the slope of the linear plot of ln (q_e - q_t) versus t.

Pseudo-Second-Order kinetics

The pseudo-second order adsorption kinetics rate equation is expressed as

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (11)$$

TABLE 1. kinetic parameters for the adsorption of As (V) onto chitosan-g-MAETC.

Sorbent	pseudo first order			pseudo second order		
	Q_e	K_1 (mg/g)	R^2	Q_e	K_2(mg/g)	R^2
CS-g-MAETC	3.01	-0.0274	0.970	17.57	0.0084	0.979

Integrated and rearranged form of this equation is

$$t / q_t = \quad t/q_e + 1/k_2 q_e^2 \qquad (12)$$

where q_e and q_t in mg/g are the adsorptive capacity at equilibrium and at time t in minutes, respectively and k_2 is the pseudo-second-order rate constant (g/mg/ min). This was calculated from the slope and intercept of the plot t/qt versus t.

The rate constants obtained from pseudo first-order (Fig.11(a)) and pseudo second-order kinetic (Fig.11(b)) models are presented in Table 1. The larger the k_1 value, the quicker is the adsorption rate, whereas the lesser k_2 value represents the faster adsorption rate[31]. The value of k_1 and R^2 did not well fit with the First-order rate model. However, the values of low k_2 and R^2suggested pseudo-second-order model. The well-fitted pseudo-second-order kinetic model predicted a chemisorptions process involving ion exchange[32]

Intra-Particle Diffusion Model

As pseudo-first order and pseudo-second order model are used to determine type and extent of adsorption but cannot identify the diffusion mechanism, the intra-particle diffusion model was used to study diffusion mechanism. Besides adsorption at the outer surface there is also possibility of intra-particle diffusion from the outer surface into the pores of adsorbent material. The adsorption mechanism of sorbate onto the adsorbent follows three steps viz. film diffusion, pore diffusion and intra-particle transport[33]. Though there is a high possibility for pore diffusion to be the rate-limiting step in a batch process, the adsorption rate parameter which controls the batch process for most of the contact time is the intra-particle diffusion. Thus in order to determine intra-particle diffusion rate constant K_p,the amount of arsenate adsorbed on the grafted polymer (q_t) was plotted against t$^{1/2}$. The rate constant for intra-particle diffusion is obtained by use of Eq. (14).

$$q_t = K_p t^{1/2} \tag{13}$$

where K_p is the intra-particle diffusion rate constant ($mg^{-1} min^{-1/2}$). In the present study the obtained intra-particle diffusion rate constant is 2.40 $mg^{-1} min^{-1/2}$.

Adsorption isotherms

Adsorption isotherms are essential for the description of interaction of solutes with adsorbents and are critical in optimizing the use of adsorbents. The equilibrium adsorption isotherms are widely employed for fitting one of the most important data to understand sorption mechanism. Several isotherm equations are available and two important models are selected for this study is Langmuir and Freundlich models[34] for the evaluation of experimental results.

Langmuir Isotherm

The Langmuir isotherm, which is valid for monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, is expressed in the linear form;

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}k_L} + \frac{Ce}{Q_{max}} \tag{14}$$

where C_e is the equilibrium concentration (ppm) and q_e is the amount adsorbed at equilibrium (mg/g). The Langmuir constants Q_{max} represents the monolayer adsorption

TABLE 2. Langmuir and Freundlich parameters for adsorption of As (V) onto chitosan-g-MAETC.

Sorbent	Langmuir isotherm			Freundlich isotherm		
	Q_{max}(mg/g)	K_L(l/mg)	R^2	n	K_f (mg/g)	R^2
CS-g-MAETC	17.9	0.18	0.997	2.6	0.56	0.873

capacity and k_L (l/mg) relates the heat of adsorption. Different Langmuir adsorption parameters obtained using Langmuir isotherm plots are given in Table 2. The linearity of isotherms and correlation coefficient values (above 0.98) support the fact that As(V) ions adsorbent data closely follows the Langmuir model of sorption over the whole concentration range studied[35]. The theoretical mono-layer saturation capacity (Q_{max}) for As (V) ions calculated from Langmuir isotherm was good agreement with the experimental values obtained for radiation grafted polymer.

Freundlich Isotherm

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The empirically derived freundlich isotherm is commonly represented by

$$q_e = K_f C_e^{1/n} \tag{15}$$

where K_f and n are Freundlich constants, characteristics of the system indicating the adsorption capacity and adsorption intensity, respectively. K_f is the predicted quantity of sorption per gram of the adsorbent at unit

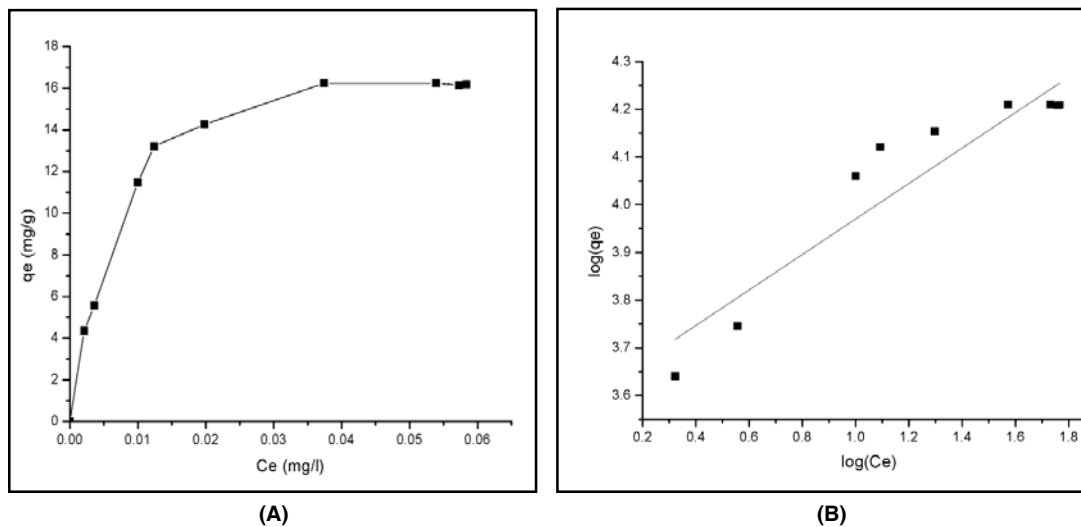**(A)**   **(B)**

Fig. 12. (a) Langmuir and (b) Freundlich isotherm

equilibrium concentration of metal ion solution and $1/n$ is the measure of nature and strength of the adsorption process as well as distribution of active sites. If $1/n<1$, the bond energies increase with the surface density, if $1/n>1$, the bond energies decrease with the surface density, and when $n = 0$, all surface sites are equivalent. Alternatively, it has been
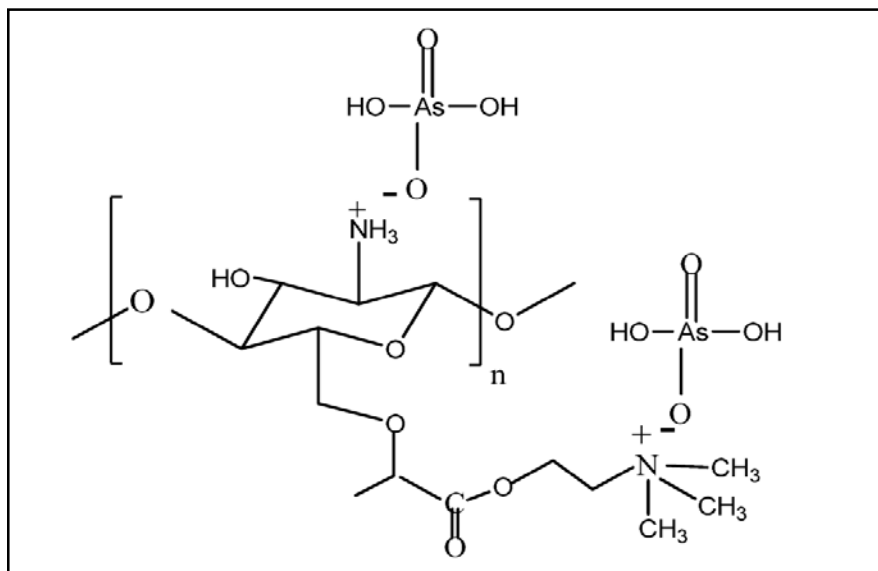
Scheme. 2. The mechanism of adsorption of As (V) onto chitosan-g-MAETC.

shown using mathematical calculation that value of n between 1 and 10, represent beneficial adsorption. To simplify the derivation of K_f and 1/n, above equation can be linearized as

$$\log (q_e) = \log k_f + \frac{1}{n} \log C_e \qquad (16)$$

The Freundlich constants, n and K_f were determined from the slope and intercept of the plot, respectively. The values of K_f and n are given in Table 2.

The essential characteristics of the Langmuir isotherm can be described by a dimensionless constant called equilibrium parameter, R_L, which is defined as:

$$R_L = 1/1 + K_L \cdot C_o \qquad (17)$$

where C_o is the initial adsorbate concentration and K_L is the Langmuir constant. The value of R_L indicates the nature of the isotherm.

Comparing the Langmuir (Fig.12(a)) and the Freundlich models (Fig.12(b)) the experimental adsorption data of As (V) ions (given in Table 2) indicated that adsorption of As (V) ions on MAETC grafted chitosan could be better explained by Langmuir adsorption model which shows a homogeneous and monolayer adsorption. Corresponding R_L values were obtained between 0 and 1 which indicate the favorable adsorption.

Mechanism of adsorption

Arsenic removal by chitosan-g-MAETC appeared to be governed by ionic interaction mechanism. As stated earlier, the arsenate ions on the oxide surface formed coordination shells with OH and NH groups through acceptance or release of H^+ at various pH, resulting in the development of a surface charge. In acidic medium, the concentration of H^+ ion remained high, and thus, chitosan-g-MAETC surface acquired positive charge, which adsorbed arsenate ions. This nature of attractive force between chitosan-g-MAETC and As(V) ions was confirmed by the FTIR results due to the appearance of new sharp peaks around 1200 and 845-500 cm^{-1} for the interaction between arsenate ion and positively charged groups in the grafted polymer [$H_2AsO_4^-$......+N-(CH$_3$)$_3$] and [$H_2AsO_4^-$ ....+NH$_3$]. With increase in pH, the surface slowly acquired negative charges, which repelled arsenate ions, and hence, arsenic removal by the electrostatic attraction in alkaline medium was ruled out. The mechanism of arsenate adsorption is shown in scheme.2.

Desorption and recycling of adsorbent

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. The effective desorption of arsenic from adsorbent can be obtained in presence of highly alkaline medium using sodium hydroxide solution, as reported elsewhere [36]. The desorption results are shown in Fig.13, which shows a gradual increase in desorption up to (98.6%) using 0.1M NaOH solution, and with increasing concentration of NaOH above 0.1M, there was no increase in desorption up to 0.3M NaOH was observed. It may be stated that, in basic medium, OH$^-$ ions compete with $H_2AsO_4^-$ ions and displace the maximum amount of adsorbed arsenic. Hence, ion-exchange mechanism is important in connection with adsorption–desorption process for adsorbent. To test the adsorption potential of regenerated adsorbent, the
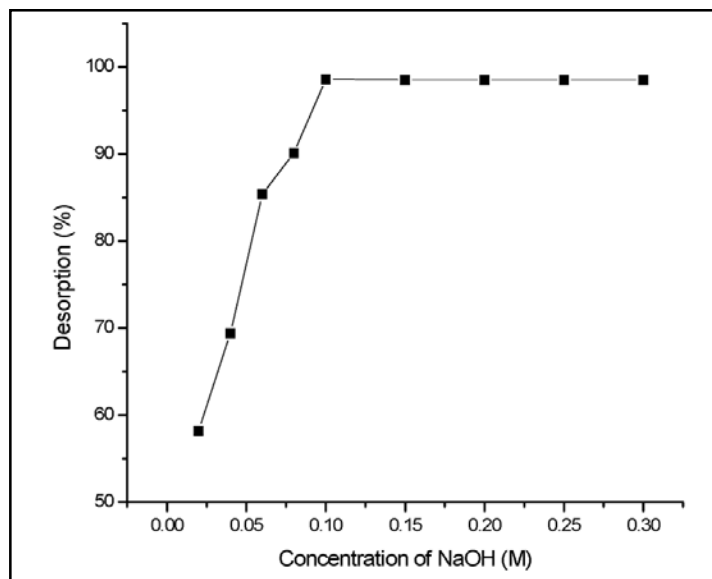
Fig. 13. Desorption of As (V) from chitosan-g- MAETC.

TABLE 3. Regeneration parameters for As (V) adsorption onto Chitosan-g-MAETC.

Adsorbent	cycles	Adsorbed amount (mg/g)	% of Removal
Chitosan –g- MAETC	1	9.5	96.7
	2	9.0	94.7
	3	8.3	92.2
	4	8.0	89.8
	5	7.2	85.7
	6	6.5	81.2
	7	6.0	78.9
	8	4.3	65.1

adsorption studies were carried out under the optimized conditions up to 8 cycles. A detailed analysis of the recycling process was performed and the results were given in Table 3. The results show that the maximum removal of As (V) was 96.7% in the 1st cycle and was found to be 78.9 % at the end of 7th cycle after which a drastic decrease in arsenic uptake capacity was noted because of the surface damage caused by the continuous process of arsenic uptake.

Application

The efficiency of the grafted polymer "chitosan-g-MAETC" for the removal of toxic arsenic ions was tested using arsenic contaminated groundwater samples collected from different parts of Rajnandgaon district, Chhattisgarh, India. The developed adsorbent applied for arsenic contaminated groundwater containing different concentrations. From this, water sample having low arsenic contamination (i.e.13.2 mg/L), 100% removal observed and increase of samples having higher amount of arsenic up to 70 mg/L, 84.3% removal was noticed. The results were shown in Table 4.

TABLE 4. Analysis of arsenic contaminated groundwater samples

Adsorbent	Sample	Before adsorption As (V) in mg/L	After adsorption As(V) in mg/L	% Removal
Chitosan –g- MAETC	1	13.2	0	100
	2	70	11	84.3
	3	50	2	96.8
	4	23	0	100
	5	45	1	97.6
	6	40	1	97.2

CONCLUSION

An extensive investigation was carried out to evaluate the arsenic (V) adsorption capacity of newly developed grafted adsorbent. The obtained results shows that chitosan-g- MAETC adsorbed maximum (17.9 mg/g) amount of As(V) compared to ungrafted chitosan (2.7mg/g) at pH 2.5-3 in 35 minutes at room temperature (25±2°C) by batch adsorption method. The adsorption mechanism followed pseudo-second-order reaction kinetics. The equilibrium adsorption isotherm data were well fitted to Langmuir adsorption isotherm. The As (V) loaded grafted sorbent was successfully desorbed using 0.1 M NaOH solution and reused for 7 times after repeated adsorption-desorption cycles. The developed grafted polymer was applied to study the removal capacity of arsenic contaminated groundwater. The adsorbent synthesized by radiation induced grating method found to be cost effective, non toxic, biodegradable and efficient adsorbent for the removal of toxic As(V) ions from aqueous solution and contaminated groundwater.

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