Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.827790

52 (2014) 6792–6801
October

Taylor & Francis
Taylor & Francis Group

Designing a cost-effective and dual-functional muslin-based anion exchanger for defluoridation

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Received 30 August 2013; Accepted 20 June 2013

ABSTRACT

In the present study, muslin was modified by graft copolymerization with poly(4-vinyl pyridine) using γ-ray initiation method. The graft copolymers, thus synthesized, were further functionalized by reaction with 2-chloroethanol. The resultant materials, having pyridinium ring and exchangeable Cl^-, were evaluated for the removal of fluoride ions from the simulated water samples. The materials exhibited high fluoride uptake and the maximum uptake was observed at pH 4.0, 20°C and 10 ppm of the fluoride ions. The maximum retention capacity of 7.7 mg/g was observed when fluoride uptake was studied up to 10 cycles. The data generated fit the pseudo-second-order kinetics and Langmuir isotherm. The efficacy of the functionalized muslin was evaluated as an antimicrobial agent against a bacterium (*Bacillus aureus*) and a fungus (*Aspergillus niger*). It was observed to be effective to inhibit the growth of both the microbes.

Keywords: Anion exchange; Anti-microbial properties; Fluoride removal; Graft copolymers; Maximum retention capacity; Muslin

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1. Introduction

Fluoride enters natural water bodies from minerals such as cryolite and fluorapatite. The presence of fluoride in drinking water up to 0.7 mg/L is beneficial to health, but is harmful at a level higher than 1.5 ppm and high fluoride contents in groundwater are common in many parts of the USA, Africa and Asia [1]. Presence of excessive fluoride, >10 ppm, in drinking water is a serious health hazard. The fluoride ions uptake beyond the safe limit adversely affects teeth and bones [2]. It is thus important to bring down the fluoride ions level to the acceptable limits. The adsorption and ion exchange processes are reported for the fluoride removal from the drinking water [3]. High rejection of fluoride ions has been reported using reverse osmosis [4–6], nanofiltration [6], anion exchange membrane [7] and electrocoagulation flotation method [8]. Different types of inorganic adsorbents and commercial resins have been reported as defluoridating materials. These include activated alumina [9], polymeric aluminium

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hydroxide [10], waste carbon slurry [11], pyrophyllite [12], tricalcium phosphate [13] and the modified Amberlite resin [14]. Adsorption kinetics of fluoride on low-cost materials has been reported [15]. Natural polymers like Zr (IV)-impregnated collagen fibre [16] and the glutaraldehyde-crosslinked calcium alginate have been recently reported as efficient adsorbent of fluoride from the aqueous solutions [17]. The modified polysaccharides are good candidates for use in the removal of toxic anion and ions [18]. The modified cellulose fibres [19], chitosan [20], have been reported as effective adsorbents for fluoride. Efficacy of the defluoridation process depends on factors like solubility, pH, temperature and the contact time [21,22]. The literature on the fluoride adsorbents is mostly limited to the anion uptake property, while the other aspects of water purification like the presence of microbes, etc., are not addressed.

In continuation to develop new materials those possess anti-microbial activity, emulsifying and water softening properties [23–25], in the present study, a new defluoridation agent based on the modified muslin is reported. Muslin (M) is a low-cost cotton fabric. It was grafted with 4-vinyl pyridine (4-VP) to obtain the functional graft copolymer, M-*g*-poly(4-VP). The later has reactive pendant pyridine moieties which were modified via reaction with 2-chloroethanol at the tertiary nitrogen of 4-VP. The functional material thus generated is dual-functional and acts both as anion exchanger and strong broad spectrum anti-microbial agent.

2. Experimental

2.1. Materials

Muslin (National Rayon Corporation, Mumbai, India), 4-VP (95%, Merck, Schuchardt, Germany), KF (97%) and 2-chloroethanol (99%, BDH, Poole, England) were used as received. Deionized water was used in all the experiments.

2.2. Synthesis and quaternization reaction of graft copolymers

Radiation grafting of 4-VP on muslin was carried out in gamma chamber by variation of different conditions such as irradiation dose, amount of monomer and water (Table 1). The maximum percent grafting (P_g) [78%] was obtained after 48 h in 5.0 ml water and 2.5 ml of 4-VP. The homopolymer was separated from the grafted muslin by extraction with methanol or equal mixture of acetone and water. The graft copolymer obtained was dried until a constant weight was obtained and was designated as M-*g*-poly(4-VP).

Candidate graft copolymers, synthesized at the maximum of different grafting conditions, were taken separately in an excess of 2-chloroethanol taking a 1:5 weight ratio of graft copolymer to 2-chloroethanol. The reaction was carried out in a temperature controlled water bath at 50°C for 36 h. Thereafter, the products were extracted with 1,4-dioxane to remove the unreacted 2-chloroethanol. The products thus obtained were dried in an air oven. FTIR spectra were recorded on Nicollet 5700 and SEMs were recorded on JEOL JSM-6380.

2.3. Defluoridation reactions: parametric study, reusability and evaluation of maximum retention capacity

The standard solution of potassium fluoride (KF) was prepared in de-ionized water. The quaternized graft copolymers were dissolved separately in the standard solution of KF. The resultant solution was treated with the SPANDNS reagent (Photolab 6600, WTW, Germany) and the concentration of fluoride anions was directly observed from the pre-programmed UV–visible spectrophotometer (Photolab 6600, WTW, Germany). The parametric study on the fluoride uptake was carried over a range of contact time (30–150 min), temperature (20–40°C), pH (2–9) and fluoride concentration (1–10 ppm) by variation of single parameter at a time. Different adsorption parameters were calculated from the following expressions:

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of fluoride ions removed}}{\text{Total amount of fluoride ions in solution}} \times 100 \tag{1}$$

Table 1
Graft copolymerization parameters of grafting of muslin by 4-VP as function of total radiation dose, monomer concentration as well as amount of water (muslin fabric = 1.0 g)

4-VP (ml)	H_2O (ml)	γ-rays dose (k Gy)*	Weight of grafted muslin (g)	P_g
1.0	10	12.528	1.16	16
1.0	10	25.056	1.33	33
1.0	**10**	**37.584**	**1.40**	**40**
1.0	10	50.112	1.29	29
1.0	10	62.640	1.27	27
1.0	10	75.168	1.26	26
0.5	10	37.584	1.25	25
1.5	10	37.584	1.42	42
2.0	10	37.584	1.47	47
2.5	10	37.584	1.52	52
3.0	**10**	**37.584**	**1.64**	**64**
3.5	10	37.584	1.60	60
4.0	10	37.584	1.55	55
3.0	**5**	**37.584**	**1.78**	**78**
3.0	15	37.584	1.61	61
3.0	20	37.584	1.58	58
3.0	**25**	**37.584**	**1.54**	**54**

Note: *Weight of muslin = 1.0 g and γ-rays dose rate = 1.566 kGy/h. Values in the bold fonts are maximum P_g recorded at the highlighted parameter.

$$\text{Partition coefficient } (K_d) = \frac{\text{Amount of F}^- \text{ removed}}{\text{Amount of F}^- \text{ remaining}} \times \frac{\text{Volume of solution in mL}}{\text{Weight of dry polymer (g)}} \tag{2}$$

$$\text{Exchange capacity } (Q) \text{ mg g}^{-1} = \frac{(C_o - C_t)V}{m} \tag{3}$$

where Q is the amount of F^- exchanged onto unit dry mass of the graft copolymer, C_o and C_t are the concentrations of ions (mg L^{-1}) in the feed solutions and after treatment for a certain period of time t, respectively. V is the volume of the solution (L) and m is the weight of dry graft copolymer used (g). Maximum retention capacity (MRC) was calculated by using the same adsorbent sample for 10 cycles and a single cycle was carried for 1 h at 20˚C and in medium of pH 4.0, using 10 ppm of fluoride ions and 100 mg of the adsorbent. MRC was calculated by the following expression [21].

$$\text{MRC} = \frac{C_m \times V}{m} \tag{4}$$

where C_m is the anion concentration sorbed by the polymer, and V is the total volume of the solution (L). The reusability studies were carried by stripping-off F^- by immersion in the saturated brine solution for 1 h and then reusing the same sample for de-fluorination.

2.4. *Antimicrobial activity of graft and quaternized copolymers*

The anti-bacterial effect of the functionalized muslin was studied by aseptically transferring the bacterial culture (*Bacillus aureus*) to the culture broth (yeast extract 0.2%, peptone 0.5%, NaCl 0.5%, beef extract 0.15% and cotton seed oil 1%, and pH 8.8) to produce the seed culture which was incubated at 55˚C with continuous shaking at 150 rpm for 30 h. The seed culture (7.5%) of the bacterial isolate was aseptically inoculated in 50 ml of the sterile production media (same as described above) containing 1% cotton seed oil as the sole source of carbon. Muslin samples were immersed separately in the seed culture. The production media flasks were incubated at 55˚C with continuous shaking at 150 rpm for 40 h. After that the cell optical density was measured at 660 nm on a UV–visible spectrophotometer (LAB India) and compared with the cell optical density of the control. The % inhibition (%*I*) was calculated on the basis of the dry cell mass (calculated from the OD) as follows:

$$\% I = \frac{\text{Cell mass of control} - \text{Cell mass of test}}{\text{Cell mass of control}} \times 100 \tag{5}$$

The anti-fungal effect of the functionalized muslin was studied by spreading *Aspergillus niger* spores in the nutrient agar plates, and the fibres were placed on these plates and then incubated at 30℃ for 40 h. Thereafter, the zones of inhibition were measured and %*I* was calculated from the following expression:

$$\% I = \frac{\text{Area inhibited by the sample}}{\text{Initial area covered}} \times 100 \tag{6}$$

3. Results and discussion

Radiation grafting is a clean and convenient method of polymer modification. In the present study, muslin was grafted by mutual irradiation method. It remains stable after grafting over the radiation dose used. A case of a high optimum graft yield of 78% was obtained by variation of different grafting parameters (Table 1). Initially, grafting increased with an increase in dose rate as more monomer radicals were generated as well as initiation sites in the form of free radicals are created on the backbone polymer. However, further increase in the dose rate results in the more homopolymer formation, hence P_g decreased. On variation of the monomer it was observed that higher monomer concentration initially promoted grafting levels but with the further increase more homopolymer formation was observed as a result of diffusion limitations, created by increasing viscosity of the medium, due to the growing monomer macroradicals to the active sites on the backbone. Increase in the amount of water beyond 5.0 mL also resulted in an increase in homopolymer formation as more radicals are formed from the water molecules and accessibility of monomer to backbone polymer is reduced [26]. Thus, optimum graft yield of 78% was obtained at 37.584 kGy with 3.0 mL of monomer and 5 mL of water.

Muslin is a low-cost cotton fabric. The graft copolymer, M-*g*-poly(4-VP), has brush-like structure with pendant poly(4-VP) groups attached to the muslin backbone [27]. The quaternization reaction of the graft copolymer with 2-chloroethanol takes place at the tertiary nitrogen of the pendant poly(4-VP) groups. While the former provides high local concentration of the pendant moieties of poly(4-VP), the latter acts both as reactant and catalyst. The reaction is very facile and the product formed is fully quaternized. The graft copolymer on reaction with 2-chloroethanol becomes dual-functional with quaternary nitrogen and Cl^- anion. The antimicrobial as well as the water softening properties of the resultant material is inherently contributed by the quaternary nitrogen, while the counter anion (Cl^-) is exchangeable [24,25]. The synthetic procedure is shown in Fig. 1.

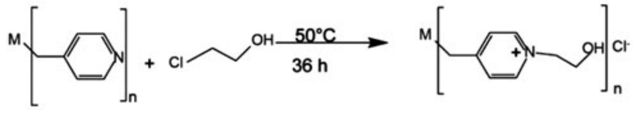


Fig. 1. Synthetic procedure.

Muslin and its different copolymeric forms were characterized by FTIR spectroscopy and SEM to obtain evidence of grafting and reaction with 2-chloroethanol. The comparison of the FTIR spectra of different polymer provides the evidence of grafting and post-functionalization of muslin and its graft copolymer to the quaternized form. The FTIR spectrum of the pristine muslin has a broad band at 3,411 cm^{-1} due to the –OH stretching. It gets depleted and it became sharper due to the loss of the hydroxyl groups of muslin which are the active sites for the grafting process. Other important band is present at 1,059 cm^{-1} due to the C–O–C stretching. Bands due to the pyridine rings

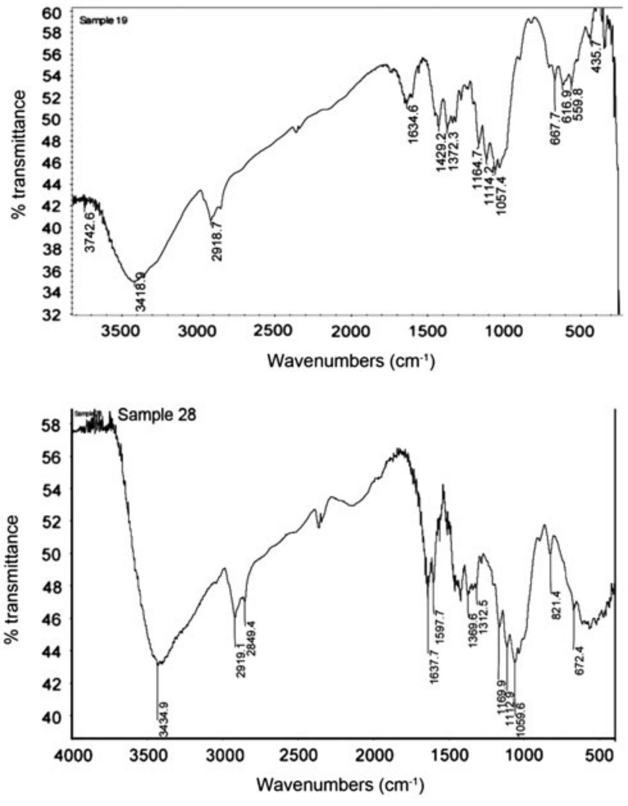


Fig. 2. FTIR spectra of (from top) M-*g*-poly(4-VP) ($P_g = 54$) and its quaternized form.

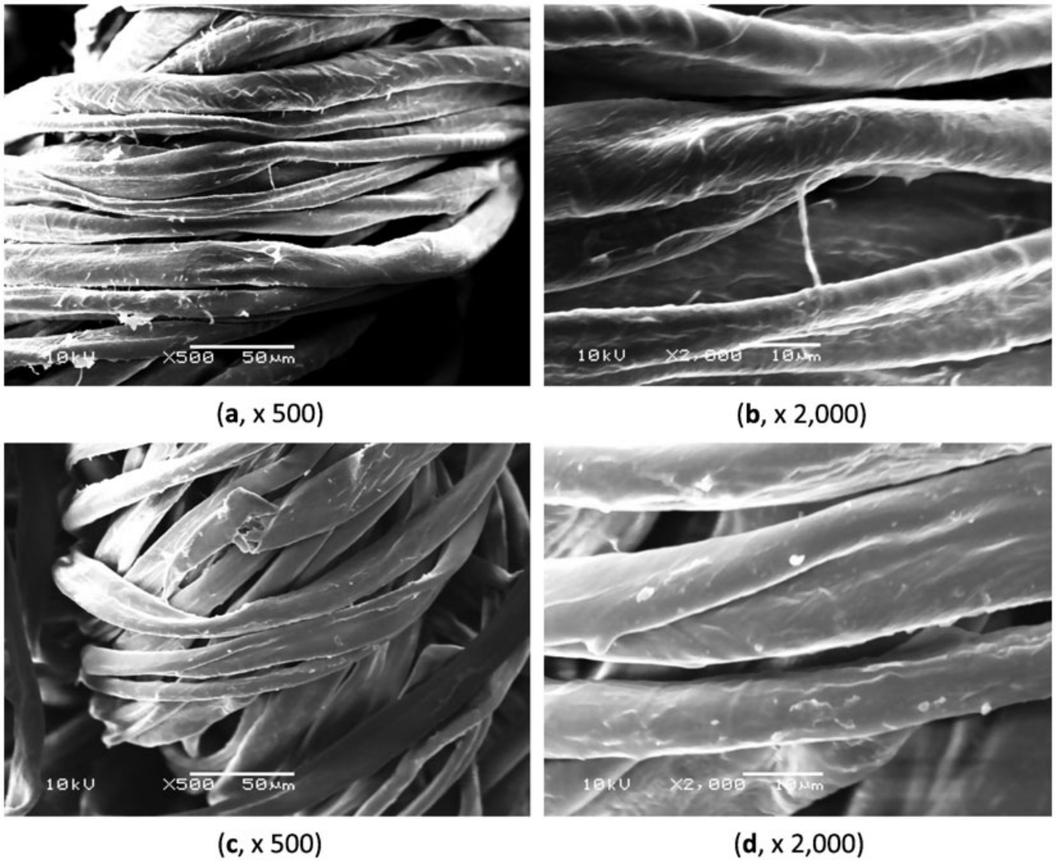
are present in the spectrum of graft copolymer at 1,634.6 and 1,429.2 cm^{-1} C=N stretching vibration and the C=C stretching vibration of pyridine ring, while strong bands appear at 1,637.7 and 1,597.7 cm^{-1} due to the pyridinium rings of the quaternized form. There is also a peak at 821.4 cm^{-1} for the substituted pyridine ring (Fig. 2). SEMs of M-*g*-poly(4-VP) and its quaternized form are presented (Fig. 3). The change in the morphology of the fibres of muslin fabric can be observed from the SEM. It is also evident that on reaction of the graft copolymer with 2-chloroethanol the thickness and shape of the fibre also changed. The fibre became thick and round shaped after grafting and quaternization reactions. There from an inference can be drawn that generation of the charged surface on quaternization changed morphology of the fibre.

3.1. Defluoridation by anion exchange: selection of candidate material

The anion exchange property of the synthesized materials emanates from the availability of the Cl^- counter anions, which are replaced by the F^- present in water. The adsorbent exhibited structure–property relationship as the candidate material with the lower P_g was observed to be more effective. The graft copolymers have brush-like shape with the muslin fabric as the backbone for the pendant poly (4-VP) chains. It is suggested that F^- exchange is limited by the density and length of the grafted poly(4-VP). Hence, the quaternized material having the highest P_g (78%) exhibited lower P_u than that which has a low P_g (54%) (Table 2). In the former, the polymeric chains are longer and more densely located. Consequently, the anions do not reach the interior of the material to replace all Cl^- due to low accessibility and electrostatic repulsion [28]. Hence, the quaternized graft copolymer with the low P_g (54.0) which exhibited the best P_u was selected for further studies.

3.2. Effect of different parameters

Effect of contact time on the fluoride uptake, presented as Q values, is presented in Fig. 4. The anion uptake process was very rapid as in the first 30 min 65.78 P_u was observed, which further increased to



(**a**, x 500) (**b**, x 2,000)

(**c**, x 500) (**d**, x 2,000)

Fig. 3. SEM images at different magnification of: (a, b) M-*g*-poly(4-VP) ($P_\mathrm{g} = 78$) and (c, d) quaternized form of (a).

Table 2
Effect of P_g on P_u and physical parameters of the resultant solution (weight of graft copolymer = 100 mg, contact time = 60 min., pH = 4, [F$^-$] = 10 ppm and temperature = 20℃)

No.	P_g	P_u	Conductivity (μ)	pH solution	TDS	Adsorption capacity (Q) (mg/g)	Partition coefficient (K_d)
1.	40	61.00	258.00	3.50	147.00	1.53	391.03
2.	54	75.00	270.00	3.44	150.00	1.88	750.00
3.	64	47.00	235.00	3.60	148.00	1.18	221.70
4.	78	31.00	215.00	3.74	146.00	0.78	112.32

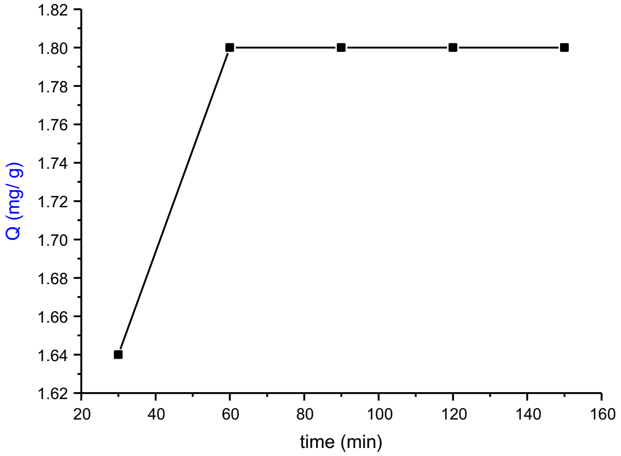


Fig. 4. Effect of contact time on Q values of F$^-$ with quaternized M-*g*-poly(4-VP) [P_g = 54] (weight of graft copolymer = 100 mg, pH = 4, [F$^-$] = 10 ppm and temperature = 20℃).

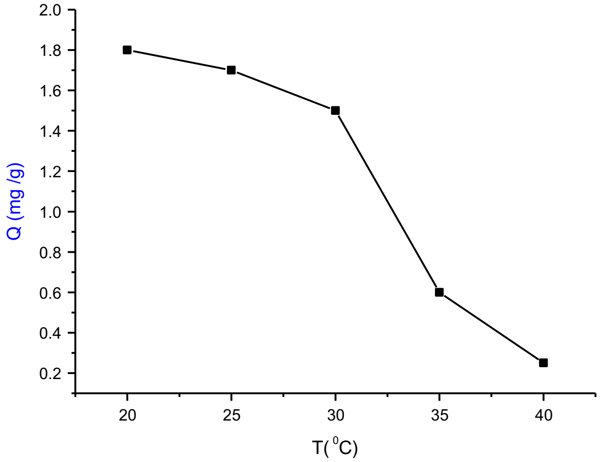


Fig. 5. Effect of temperature on Q values of F$^-$ with quaternized M-*g*-poly(4-VP) [P_g = 54] (weight of graft copolymer = 100 mg, pH = 4, [F$^-$] = 10 ppm and time = 60 min).

75% after 60 min. Thereafter, it remained constant due to the low availability of the F$^-$ at the concentration studied. Such observed behaviour has technological significance for use of these materials in water technology. It is reported in literature that the F$^-$ uptake, after an initial rapid and high uptake, decreased and then remained constant with time [19]. The effect of temperature on the F$^-$ uptake was studied from 20℃ to 40℃. Q was observed to decrease with an increase in temperature. The F$^-$ uptake is an exothermic process [20]. An increase in temperature beyond 20℃ decreased P_u to 10 at 40℃ (Fig. 5). The effect of pH of the medium is presented in Fig. 6. A slow decrease in the adsorption capacity with an increase in pH has been reported [19]. In the present case also the same trends were observed. At the low pH, the pyridinium ions on the graft chains and the positively charged ions in the medium repel each other, and result is the opening of the polymer matrix. Such interactions resulted in the better accessibility of the F$^-$ to N$^+$ where the counter anion Cl$^-$ is present. The argument is also supported by the fact that the graft copolymer swells maximum in water at pH 2.0. An increase in the feed concentration of F$^-$ has a positive effect on

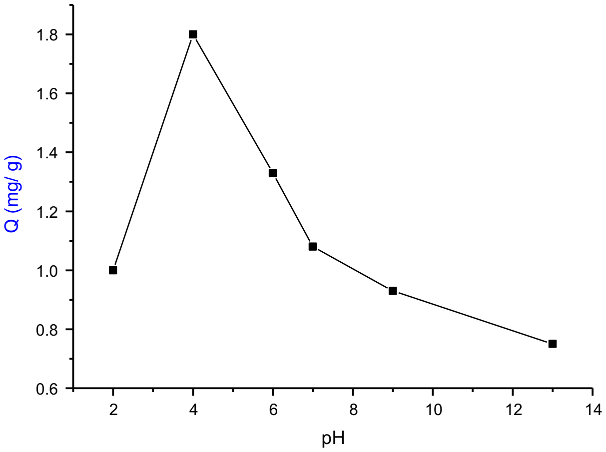


Fig. 6. Effect of variation of pH on Q values of F$^-$ with quaternized M-*g*-poly(4-VP) [P_g = 54] (weight of graft copolymer = 100 mg, contact time = 60 min, and temperature = 20℃, and [F$^-$] = 10 ppm).

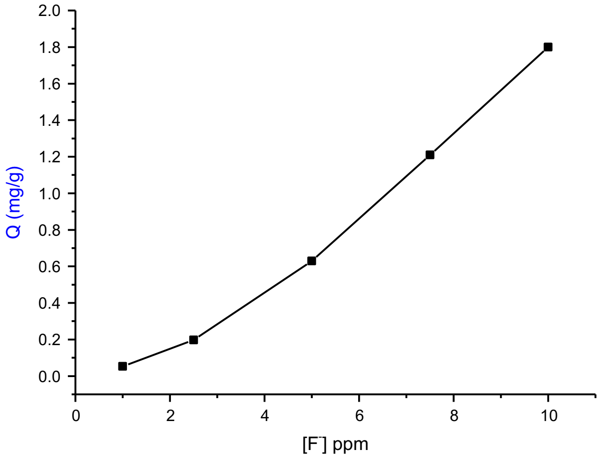


Fig. 7. Effect of variation of F^- feed concentration on Q values with quaternized M-*g*-poly(4-VP) [$P_g = 54$] (weight of graft copolymer = 100 mg, contact time = 60 min., pH = 4 and temperature = 20°C).

the adsorption capacity of the adsorbent as it increased almost linearly with an increase in the F^- concentration in the solution (Fig. 7). The steady increase in Q values with an increase in the anion concentration means that the modified muslin is capable of even taking up more anions at the higher concentration range.

3.3. Evaluation of MRC and reusability studies

The best performance of the anion exchanger (using 100 mg) was observed at pH 4.0, 20°C and 10 ppm of F^- anions (the maximum of the range studied). MRC was evaluated by repeatedly using the same material for 10 cycles, and the MRC of 7.7 mg/g was obtained (Fig. 8). Since MRC is the total experimental capacity of the ion exchanger, Q value obtained from each experimental cycle was added to obtain the cumulative Q value. Hence, the Q values exhibited an increase with the number of cycles till the near saturation was achieved. It corresponds to 0.41 meq/g. MRC obtained is 78.79% of the theoretical value of the active sites present. Desorption of F^- was achieved by treating the F^--loaded material with the NaCl solution, and the material was found to be reusable in many treatments (Fig. 9). The exchange capacity or Q value was plotted individually for the successive cycles. A decrease in Q values is result of lack of total exchange of the F^- ions due to the accessibility of the Cl^- to reach all the active sites. The result is availability of lesser sites for the next step, hence decrease was observed in Q values. The exchange capacity in the present case is very high compared to other materials of different sources reported in literature with value of 2.31 [29], 5.16 [30], 6.0 [31] and 3.1 [32] mg/g.

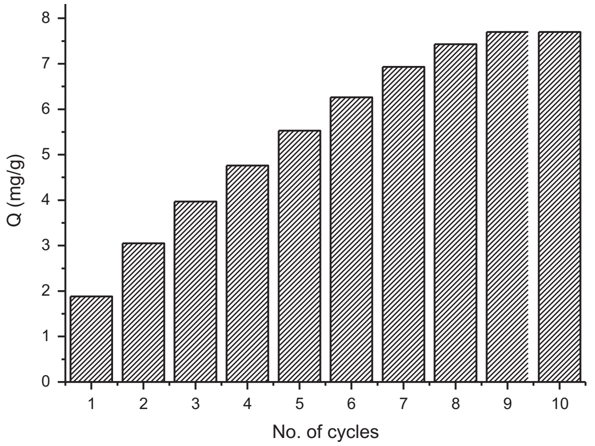


Fig. 8. MRC after six feeds of F^- solution with quaternized M-*g*-poly(4-VP) (weight of graft copolymer = 100 mg, contact time = 60 min., pH = 4, [F^-] = 10 ppm and temperature = 20°C).

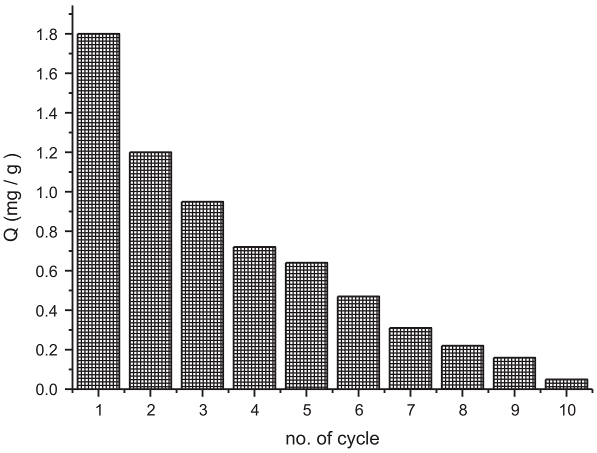


Fig. 9. Reusability of regenerated quaternized M-*g*-poly(4-VP) (weight of graft copolymer = 100 mg, contact time = 60 min., pH = 4, [F^-] = 10 ppm and temperature = 20°C).

3.4. Mechanism of ion exchange and evaluation of the applicability of the adsorption isotherms and kinetic models

Muslin is a biodegradable, cost-effective, hydrophilic and porous material that provides support to the active chains of graft copolymers and their quaternized forms. Muslin itself and its modified forms are good water absorbent. Hence, by interacting with water, the ionic species are also partitioned to the backbone and anchored at the opposite charged sites of the material. The anions are adsorbed on the quaternary nitrogen of the pyridinium moieties of the

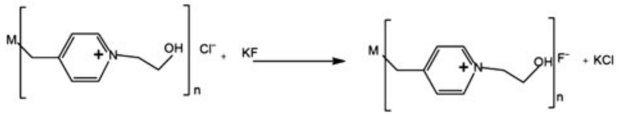


Fig. 10. Anion exchange.

grafted chains. The anion exchange manifested in the removal of fluoride is illustrated in Fig. 10.

As expected in anion exchange mechanism, parameters such as pH, total dissolved solute (TDS) and conductivity of the resultant solution were observed to vary with the Q or the K_d values (Table 2). The later is dependent both on the nature of the ion and the adsorbate. The adsorption isotherm plays an important role in the determination of the mechanism of the ion uptake. In order to evaluate the same, the Langmuir and Freundlich isotherm equations were considered using the relationship reported elsewhere [18]. Whereas the former assumes a weak physical sorption of the ions on a surface with homogeneous adsorption, the later is a non-ideal sorption that involves heterogeneous adsorption over the active sites. The Langmuir adsorption isotherm exhibited better correlation than the Freundlich adsorption isotherm with a R^2 value of 0.9989 and in the latter it is far lower. Such behaviour is expected from a mechanism where exchange of anions is the predominant process. The figures for both the isotherms have been presented as Fig. 11. Similar result is reported elsewhere [31,32]. The applicability of the pseudo-second-order kinetic model in this case signifies the anion exchange mechanism. It was found to be applicable over the whole range of the contact time (Fig. 12, inset). As aforesaid, this mechanism is also supported by the observations that after the completion of the experiments the pH and other parameters of the resultant solution were found to be different than the initial values.

3.5. *Anti-microbial behaviour of the graft copolymers and functionalized forms*

Anti-microbial properties exhibiting polymers have quaternary ammonium moieties those are of biocidal nature. In the present case also the functionalized fabric have strong antimicrobial activity due to the presence of pyridinium ions. These kill microorganisms or inhibit their growth. In the present case since the fabric are not soluble, hence its anti-microbial action was studied by the zone inhibition studies. That means bacterium or fungus does not grow in the presence of polymer. Anti-microbial behaviour of the graft copolymers and their functionalized forms was evaluated against *B. aureus* and *A. niger*. The as-synthesized graft copolymer was used as control. It did not exhibit any anti-microbial activity. That implies that the presence of pryridinium ions is vital for the antimicrobial action [25]. The antimicrobial action results from the disruption of the cell walls of the microbes when these come in contact with the functionalized muslin. The potency of these materials as the antimicrobial agents is evident from the fact that the maximum %*I* of 77.1 and 80, respectively, was observed for the anti-bacterial and anti-fungal action (Fig. 13). Both these properties are almost independent of the graft levels. It means that the anti-microbial action is a surface phenomenon that resulted by the interaction between the microbes and the material [25].

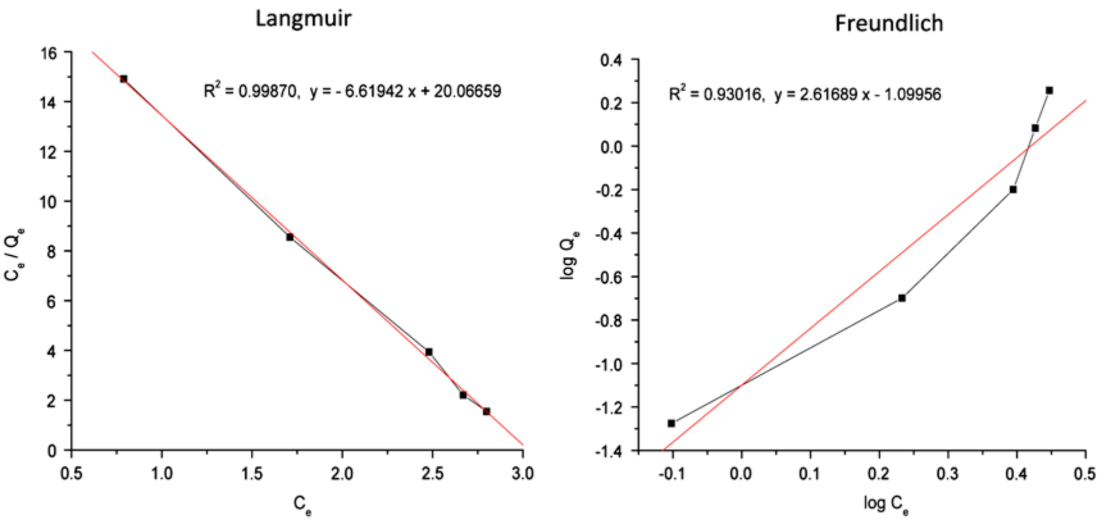


Fig. 11. Langmuir and Freundlich isotherms.

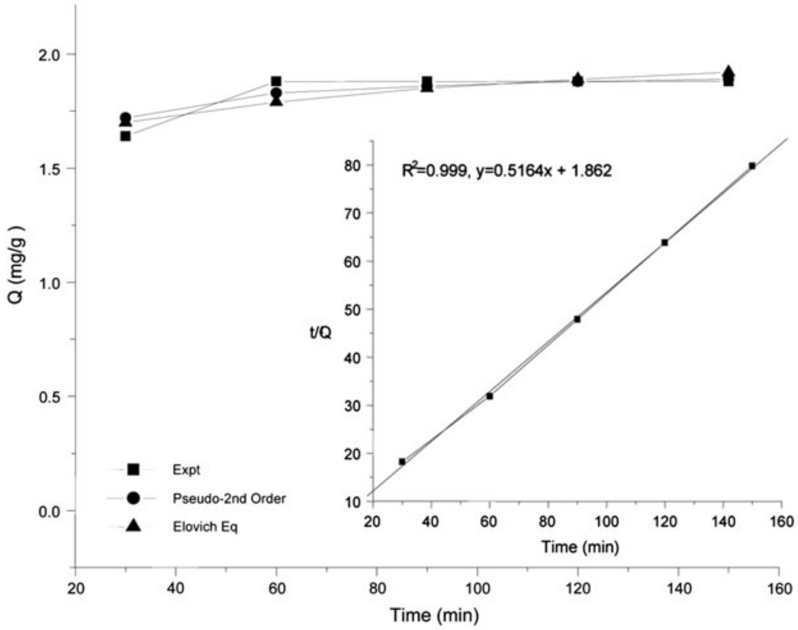


Fig. 12. Match of the kinetics of F^{-} removal using pseudo-second-order and Elovich equation (inset, linear fit of pseudo-second-order values, $t/_Q$ vs. t (min).

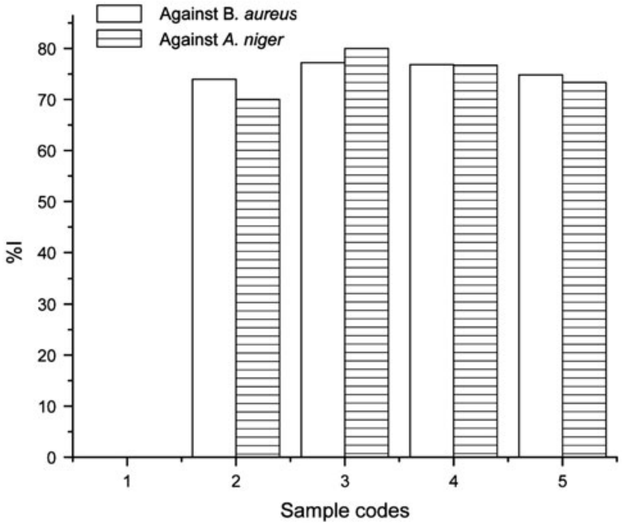


Fig. 13. % Inhibition by different quaternized M-*g*-poly(4-VP) against *B. aureus* and *A. niger* (1 = muslin, 2,3,4 and 5, respectively, graft copolymers with initial $P_g = 40$, 64, 78 and 54).

4. Conclusions

New cotton-based materials were synthesized from muslin and poly(4-VP) by γ-ray initiation method. The grafted muslin was further functionalized to choline analogous materials. The resultant materials obtained are of dual-functional nature having anion exchange and anti-microbial properties. These were evaluated as supports for the removal of fluoride ions from the simulated water samples. The anion uptake was observed to be dependent on the pH, temperature and fluoride ions concentration and followed exchange mechanism. The data generated fit the Langmuir isotherm and pseudo-second-order kinetics. The materials also exhibited strong anti-microbial properties against both bacterium and fungus. Thus, the materials reported are low cost, efficient anion exchanger and strong antimicrobial agents and have technological potential for use in water technologies.

Acknowledgement

Sunil Kumar is thankful to the Government of Himachal Pradesh, India, for the sanction of study leave.

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