Study of radiation induced grafting of [(methacryloylamino)-propyl] trimethyl ammonium chlorite (MPTAC) on to cotton fabrics and its application

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ABSTRACT

Quaternary ammonium salt, [(methacryloylamino)-propyl] trimethyl ammonium chlorite (MPTAC) had been used as monomer in mutual radiation grafting process on cotton fabrics with the aid of high energy gamma radiation source. The polymer chains of MPTAC were successfully grafted covalently onto cotton fabrics. Effect of selected experimental variables such as irradiation dose, monomer concentration, and ambient conditions and effect of inhibitors on extent of grafting had been analyzed. Grafting yield increases steadily with monomer concentration. The highest grafting yield obtained at 2kGy and reduces thereafter then become almost constant at higher dose range. The grafted samples characterized for its surface morphology. Finally the grafted cotton subjected to its dye uptake capacity and antibacterial efficacy. The grafted cotton fiber was used in absorption studies of aqueous basic dye solution, namely AB74. The grafted cotton posses very good dye uptake capacity. The maximum dye uptake capacity of the grafted cotton sample was 150mg/g. Antibacterial efficacy has been tested by qualitative and quantitative methods against model bacteria S. aureus and E. coli from gram positive and gram negative respectively. 20% grafted cotton was found to be responsible of 2 log cycle reductions for the E.coli and S.aureus colonies.

ABSTRAK

[(Methacryloylamino)-propyl] trimethyl ammonium klorida (MPTAC) telah digunakan sebagai monomer dalam proses cantuman radiasi bersama pada serat kapas dengan radiasi gamma. Rantai polimer MPTAC telah berjaya dicantumkan ke atas serat kapas secara ikatan kovalen. Kesan pembolehubah eksperimen terpilih seperti dos penyinaran, kepekatan monomer, keadaan ambient serta kesan inhibitor pada tahap cantuman telah dianalisa. Hasil peningkatan cantuman berkadar terus dengan kepekatan monomer. Hasil cantuman tertinggi diperolehi di 2 kGy dan berkurang selepas itu serta kemudianya menjadi hampir malar pada dos yang lebih tinggi. Sampel jerat kapas diuji morfologi permukaan. Akhirnya sampel tertakluk kepada kapasiti pengambilan warna dan ketahanan anti-bakterianya. Jerat kapas memiliki kapasiti pengambilan warna yang sangat baik. Pengambilan kapasiti maximum adalah 150mg/g. Ujian kinetik mendedahkan bahawa serat dengan hasil cantuman sebanyak 15% mampu untuk menjerap warna pada kepekatan 200ppm dalam masa 5 minit. 20% kapas dicantumkan didapati 2 log pengurangan kitaran untuk bakteria E.coli dan S.aureus.

Keywords: Mutual Radiation Grafting, Gamma radiation, Grafting Yield, Surface Morphology, Thermal Stability

INTRODUCTION

Polymer surfaces can be modified to achieve a variety of goals, including increasing adhesion, improving wettability and biocompatibility, reducing friction, reducing susceptibility to harsh chemicals or environmental agents, bio-functional surfaces in tissue engineering functional adsorbents and antibacterial surfaces (Kumar et al. 2005). Polymer surfaces may also be modified by functionalization with various chelating groups for their application in the treatment of waste water, such as toxic metals and dyes from textile effluents to address the serious environmental pollution problem (Goel et al. 2011). There are a number of existing physical and chemical surface modification methods are available, such as conventional thermo-chemical methods, high energy radiation, UV, plasma, enzymatic and laser based methods. However, high energy radiation (gamma-ray, electrons beams etc.) based technology offers unique advantages over other processes, such as environmental friendly, easy, convenient, efficient process that provides the high purity product with uniform and high degree of functionalization.

An ultimate interest has grown on radiation induced surface modification by grafting copolymerization technique lately due to huge benefits driven by economically and indefinite efficiency without chemical initiation (Ma et al. 2011). Cotton widely used as clothing materials due to its natural abundance (Gowariker et al. 1999) However, one of the most spotted disadvantages of this material was the vulnerability towards bacterial and fungal attack. Thus, radiation grafting method has been adopted to modify cotton cellulose fiber to enhance its physicochemical properties due to distinctive advantages over conventional chemical grafting (Garnett, J.L., 1979).

[(Methacryloylamino)-propyl] trimethyl ammonium chloride (MPTAC) monomer a well known quaternary ammonium salts, have been chosen for grafting on to cotton fabrics. The potential of quaternary ammonium compounds as antimicrobial agents, make their application possible in domestic, industrial and clinical appliances. Besides that, the PMPTAC-g-cotton samples were tested for their dye adsorption capacity as well. Synthetic dyes were actively being used in various manufacturing businesses such as textile, printing, plastics and leather (Mei et al. 2012)(Zollinger, H., 1987). The effluent discharged from all these industries would contain high amount of recalcitrant dyes and release of this wastewater into stream is unethical and will lead to serious environmental issues. In the present study, radiation grafting of [(Methacryloylamino)-propyl] trimethyl ammonium chloride (MPTAC) on to cotton fiber was carried out wherein, experimental parameters like total dose, monomer concentration, effect of additives etc have been studied. The PMPTAC-g-Cotton samples were further tested for antimicrobial activity and as an adsorbent for the acid dyes.

EXPERIMENTAL

Materials

The cotton fabrics used in this study was purchased from local vendors. The finished cotton fabric disassembled into fibrous form and washed with ethanol for 5 hours followed by 1 hr treatment with 1% sodium hydroxide solution in order to remove the impurities presents. The treated fibres washed thoroughly with distilled water until neutral washing attained. The prepared fibre samples dried in oven at 50^0C prior to storage in desiccator for further usage. MPTAC (Mol wt. = 374.34 in the form of 50% aqueous solution, from Aldrich) was utilized without further purification. All other chemicals used were AnalaR (Purity > 99%) grade. Doubled distilled water was used for sample preparation and also as an extractant for the removal of homo-polymer from the grafted samples. The Acid dye Acid Blue74 (AB74) from Sigma–Aldrich was used as a model dye for adsorption study.

Methods

Synthesis of PMPTAC by gamma irradiation

Linear poly{[(Methacryloylamino)-propyl] trimethyl ammonium chloride}(PMPTAC), was synthesised by irradiating 10%, 15% and 30% aerated aqueous solution of MPTAC by ^{60}Co gamma radiation source with total absorbed dose 5 kGy at dose rate of 2kGy.h^{-1}. The irradiated samples were precipitated multiple times in excess of acetone in order to remove the monomer and oligomers from polymer form by irradiation.

Radiation Grafting of PMPTAC on to cotton fabric

Grafting of MPTAC onto cotton fibres was carried out by mutual irradiation technique using ^{60}Co gamma radiation in a gamma chamber (GC 5000, BRIT Mumbai, India) at dose rate of 2.0 kGy h^{-1}. The dose rate was determined by Fricke dosimeter. Briefly, the known weights of dried cotton fibre samples were immersed into MPTAC solution of desired concentration taken in stoppered glass vials followed by gamma irradiation for required radiation doses. The irradiated samples were then washed with doubled distilled water and continuously rinsed with hot water multiple times to remove physically adsorbed homopolymer on surface of PMPTAC-g-Cotton fibres. The PMPTAC-g-Cotton samples were dried in vacuum oven at 50^0C and grafting yield (%) determined gravimetrically by following equation (1):

$$\text{Grafting yield (\%)} = \frac{\text{Weight after grafting} - \text{Initial weight}}{\text{Initial weight}} \times 100$$

Fourier transform infrared analysis (FTIR)

Functionalization of cotton fibres carried out by radiation grafting method was confirmed by Fourier transformed infrared (FTIR) analysis, performed on an IR Affinity-1 spectrometer (Shimadzu, Japan) in diamond single reflectance ATR mode. FTIR spectra were recorded in the range from 400 to 4000 cm^{-1}, with a resolution of 4 cm^{-1} and averaged over 50 scans.

Scanning Electron Microscope (SEM)

Morphological analysis of the samples was performed with Scanning Electron Microscopy (SEM) using FEI Quanta 400. Bio Rad coating system was used to sputter gold onto the samples under vacuum condition. Ungrafted cotton, grafted cotton with yield of 5% and 27% was subjected to this analysis for observation on morphological changes as effect of radiation grafting process.

Elemental analysis

Elemental analyzer model, Flash EA-112 from Thermofinnigan, Italy has been used to determine the nitrogen content of PMPTAC-g-cotton cellulose matrix. The nitrogen content of samples with different grafting yields was determined and correlated with grafting yield calculated gravimetrically.

Antibacterial tests

Quaternary ammonium salts are well known antibacterial compounds and used in many liquid medicines as an inhibitor to the growth of microorganism like bezalkonium chloride in eye drop/ear drop solutions. Antibacterial nature of QUATs was found in close correlation with length and nature of alkyl groups in QUAT. MPTAC is another monomer which is structurally different from early studies QUATs like VBT, MAETC, and AETC. MPTAC is having relatively more polar alkyl group because of amide group. Therefore, antibacterial efficacy has been tested by qualitative and quantitative methods against model bacteria *S. aureus* and *E. coli* from gram positive and gram negative respectively. In qualitative methods, agar well method has been adopted. PMPTAC solution of appropriate concentration have been put in the well and incubated for 24hrs at 37^{o}C. Depending upon the antibacterial efficacy, it will not allow the growth of the bacterium and will form the zone of inhibition. Secondly, only gram positive *S. aureus* have been taken for preliminary quantitative studies by plating method. Grafted sample with ~20% grafting extent was taken in to suspension of test bacterium and aliquots were taken after 1, 2, 4 and 6 hour interval.

Adsorption Test

The stock solution of dye at concentration 1000 mg/L was prepared using double distilled water. The stock solution diluted to desired concentration for adsorption study. Known weight of PMPTAC-g-cotton samples with particular of grafting yield was immersed in 50ml of dye solution with ascertain concentration in stoppered conical flask. UV/Vis spectrophotometer (Evolution-300, Thermoelectron Corporation, Ltd., UK) was used to estimate to concentration of dye solution after adsorption process with calibration curves at wavelength which corresponds to maximum absorbance, i.e., λ_{max} = 610nm for dye AB 74. The amount of dye adsorbed was calculated with equation (2) shown below.

$$q_e = \frac{(C_i - C_e)V}{m.1000}$$

Where C_i and C_e represent the initial and final concentration of dye after adsorption, V (mL) is the volume dye solution and m (g) is the mass of grafted cotton fibres used.

RESULTS AND DISCUSSION

Effect of dose

The effect of irradiation dose on grafting yield was studied on 20% of MPTAC aqueous solution at varying doses from 0.25 kGy to 8.5 kGy. The dose rate used throughout this study was 2 $kGyh^{-1}$. The grafting yield increases drastically with irradiation dose up to 2 kGy then reduced and become almost constant at higher dose range, as shown in Fig. 1. An increase in irradiation dose will leads to formation of more active radicals sites on trunk polymer which offers more chances for monomers to be grafted on the cotton backbone. In mutual radiation grafting system, the grafted chains numbers and length directly related to irradiation dose (Chapiro, A., 1962). Therefore, this explains the concept of relationship between grafting yield and irradiation dose. The sudden increase in the grafting yield with the radiation dose with the appearance of a peak can be explained by a well known 'Trommsdroff effect', an auto-acceleration effect induced by increasing viscosity due to polymer chain growth. This effect is explained by the lower mobility of the propagating chains in viscous media, resulting in lower termination rates because of diffusion limitations operating in the system (Trommsdorff et al. 1948)(Farquet et al. 2007).

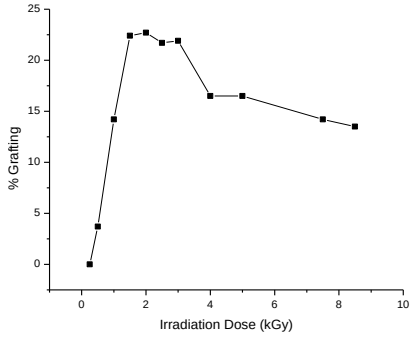

Fig. 1. Effect of irradiation dose on grafting, (MPTAC)=20% (w/w) in water, aerated solution.

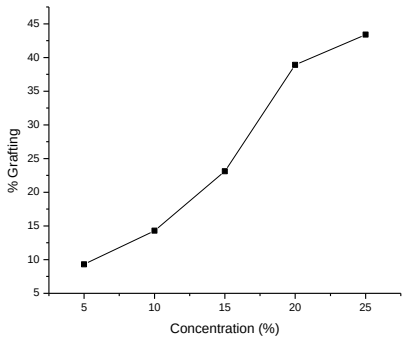

Fig. 2. Effect of monomer concentration on grafting. Total dose 5 kGy under aerated condition

Effect of monomer concentration

The grafting was carried out at different concentration of MPTAC in order to study the effect on grafting yield. The irradiation dose was fixed to 2kGy. Volume of solution with the substrate weight ratio maintained at constant under aerated condition. The results of this variable are shown in Fig. 2. Within the concentration range studied, the grafting yield shows increasing trend with increase in the monomer concentration. By the existence of additional monomers, the active radical sites formed on polymer backbone able to have more interaction with monomers which gives higher grafting yield instantly. Anyhow, formation of homopolymers also will be ideally preferable as bulk generation of monomer radicals at higher concentration of monomer (Khattri, S.D. and Singh, M.K., 2000). Thus, the concentration of monomer fixed at 20% (w/v) to attain high level of grafting and negligible amount of homopolymer formation for further parameter analysis.

Effect of ambient condition

The effect of ambient condition on grafting as the function of monomer concentration and dose was examined in this study. The grafting was done under three different ambient conditions: N_2 purged, aerated and O_2 saturated. The results achieved shown in Fig.3. and Fig.4. Lower grafting yield obtained in present of oxygen in comparison to aerated and N_2 purged condition for both variations in dose and monomer concentration. The radical scavenger nature of O_2 hinders reaction initiated by radicals is responsible for the results (Spinks, J.W.T. and Woods, R.J., 1990). Basically, the cellulose backbone of cotton fabrics is highly porous in nature where dissolved oxygen could easily diffuse into it and able to quench the active radicals formed on the surface by irradiation which might be responsible for the reduction in grafting level. It could be also seen that the induction

dose of 0.5 kGy and 1.5kGy was observed for aerated and O_2 saturated monomer solution, respectively (Fig 4). Since the difference in grafting yield between N_2 purged and aerated condition insignificant, remaining grafting experiments were carried out at aerated condition for simplicity.

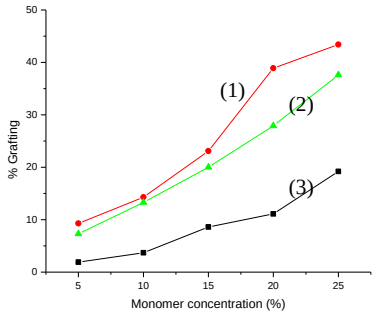

Fig. 3. Effect of ambient on grafting different concentration of monomer). Total dose 5 kGy and volume of solution 5mL. (1) N_2 purged, (2) Air and (3) O_2 saturated

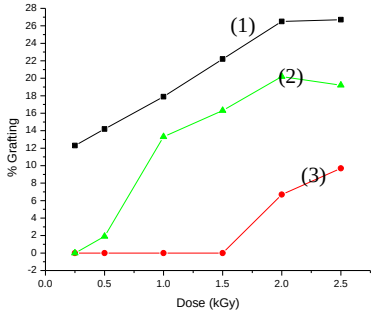

Fig. 4. Effect of ambient on grafting (different dose). Total dose 5 kGy, (MPTAC) = 20% (w/w) in water and volume of solution 5mL. (1) N_2 purged, (2) Air and (3) O_2 saturated

Effect of homopolymerization inhibitors

A major disadvantage of mutual grafting process is the generation of unwanted homopolymer during the grafting process, and special extraction technique need to be employed to remove those unnecessary by-products. It has been well known that addition of small amount of metallic salts to sample mixture would inhibit the homopolymer formation by increasing the availability of monomer free radicals for grafting reaction and also simplify the recovery of copolymer formed (Gargan et al, 1990)(O'Nell, T., 1972). Therefore, suppression of homopolymer formation was studied by addition of well known homopolymer inhibitor agent, namely Mohr salt ($FeSO_4.(NH_4)_2SO_4.6H_20$) and $CuSO_4.5H_2\ SO_4$.

Three different systems were studied to discover the effect on grafting yield. Mohr salt ($FeSO_4.(NH_4)_2SO_4.6H_20$) was added to the first system and the second system was made up with Mohr salt with 0.1M H_2SO_4. Whereby the third system comprises only $CuSO_4.5H_2\ SO_4$ and the results displayed in Fig. 5. It was found that the formation of homopolymer was also decreased in presence and by mean of all the systems shows reduction in grafting level but grafting was inhibited totally in the system only with $CuSO_4.5H_2SO_4$. During irradiation, radiolysis of water will take place and hydroperoxides formed on polymer backbone also will decompose which will generate OH radicals in bulk. The conversion of these OH radicals to non-reactive OH anions (Eqs.3A-C) would be responsible for the reduction in homopolymers (Goel et al.2013). The observation support that presents of Mohr salt in MPTAC-cotton fiber system controls the formation of homopolymer with the severe compromise on grafting yield. The cotton fibers in Mohr salts found to be slightly yellowish in color due to adsorption of Fe^{2+} ion by the substrate. Metal ions well known radical sites deactivator and this nature might be liable to reduction in grafting by termination of growing grafting chains (Steenken, S., and Neta, P., 1982). The adsorption of Cu^{2+} by cotton during reaction may hinder the grafting when the system mixed with $CuSO_4.5H_2\ SO_4$ and therefore no grafting gained in this particular system.

$$H_2O \longrightarrow {}^{\cdot}OH + {}^{\cdot}H + e^-_{eq} + H_2 + H_2O_2 \quad \text{..... (3A)}$$

$$ROOH \longrightarrow {}^{\cdot}RO + {}^{\cdot}OH \quad \text{..... (3B)}$$

$$Fe^{3+} + {}^{\cdot}OH \longrightarrow Fe^{2+} + OH^- \quad \text{..... (3C)}$$

Some of previous studies had concluded that present of acid in system will enhance the grafting yield (Dworjanyn, P.A. and Garnett, J.L., 1989)(Chappas, W.J. and Silverman, J., 1979). But it is not applicable in this work as sharp reduction observed in grafting with addition of acid.

Effect of organic solvents

Grafting was performed in series of alcohols to study the impact on grafting since radiation grafting depends on type and composition of solvent used in the mixture. Among of the four alcohols used only Butanol show an increasing trend in grafting and the rest shows decreasing order (shown in Fig. 6). The trend of grafting yield was butanol > propanol > ethanol > methanol. There are three different approach of solvents effect the grafting level. Solvent behave as a good swelling agent at polymer backbone (Dilli et al 1972). This will make the approach of monomer to active sites easier and promotes grafting. Solvent can act as an efficient chain transfer agent whereby they capable to quench the active sites formed on polymer body which eventually causes reduction in grafting or grafted chain length (Lawrence, K.D.N. and Verdin, D., 1973). Grafted polymers which are insoluble with solvent could turn into globular shape in order to avoid interaction of active sites on growing chains with monomers cause reduction in grafting (Bhattacharya, A. and Misra, B.N., 2004). Methanol are small in size comparable to other alcohols hence possibly methanol diffuse into cotton fibres and may quench the active sited formed on substrate. This owes the rationalization for lowest grafting yield observation with the present of methanol in general. Predomination of chain transfer efficiency over wetting abilities of solvents makes the grafting extent reduces with existence of alcohols. Researchers experienced same outcome in previous studies as well (Badawy et al. 2005). Little amount of grafting was gained in pure solvent (without water), which signify the importance of water in grafting system. Sum of free radicals ($^{\cdot}H$ and $^{\cdot}OH$) from radiolysis of water will be very less with the absent of water which will abbreviate the active sites on cotton backbone.

However, opposite phenomenon noticed in the case of butanol. The grafting yield linearly related to composition of butanol in system. Butanol is less polar and bigger molecule among all the solvent been used in this study, however, it shows higher chain transferring efficacy. Thus, the although the wetting ability of butanol for cellulose would be lesser than the rest of the other solvents, its diffusion to the cotton fibril backbone will be less and so may quench the reactive sites at the backbone to the lesser extent, leading to the increase in grafting yield. Moreover, as the chain length increase, wetting ability solvents generally decreases which hinder formation of homopolymer and increase monomers availability for grafting.

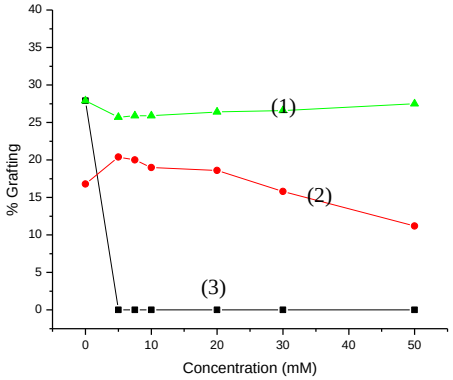

Fig.5. Effect of metal salts and acid on grafting. (MPTAC)=20% (w/w), total dose 2kGy under aerated condition. 1)$FeSO_4.(NH_4)_2SO_4.6H_20$, 2)$FeSO_4.(NH_4)_2SO_4.6H_20 + H_2SO_4$, 3) $CuSO_4.5H_2SO_4$.

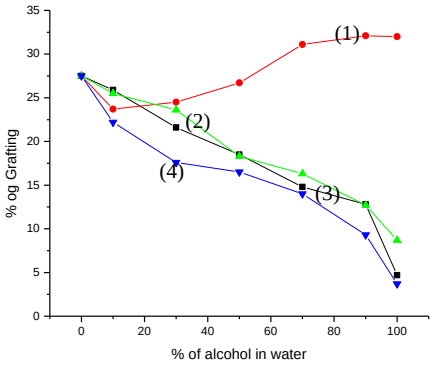

Fig.6. Effect of solvent composition on grafting. (MPTAC)=20% (w/w), total dose 2kGy under aerated condition. 1) Butanol, 2) Propanol, 3) Ethanol and 4) Methanol

Characterization of grafted cotton

Elemental analysis

In order to determine the amount of nitrogen present in grafted samples, elemental analysis was performed as MPTAC monomer contains one nitrogen atom in quaternary ammonium group. The samples displays linear trend for nitrogen content as grafting extends of samples increases (shown in Fig. 7.). This observation clearly

agrees that cotton fibres had successfully grafted with MPTAC monomer and amount of nitrogen was detected on cotton samples increases with grafting extent.

FTIR analysis

FTIR analysis performed on virgin cotton, grafted cotton and radiation polymerized MPTAC. Fig.8. displays the FTIR spectrogram of specified samples. Additional peaks had obtained for PMPTAC and MPTAC-g-cotton samples; peaks at ~1650 cm^{-1} and ~1540 cm-1 for secondary amide carbonyl stretching and N-H bending, respectively, and ~1475 cm^{-1} for δ(–N+(CH3)]. Incorporation of MPTAC with cotton cellulose structure was confirmed by present of these peaks.

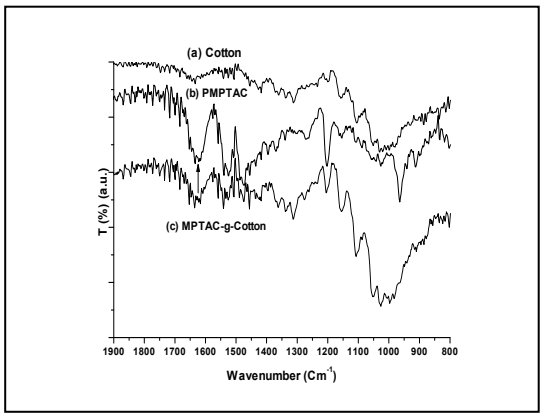

Fig.8. FTIR Spectra of (a) Control cotton (b) Poly-MPTAC and (c) MPTAC-g-cotton (GY=30%)

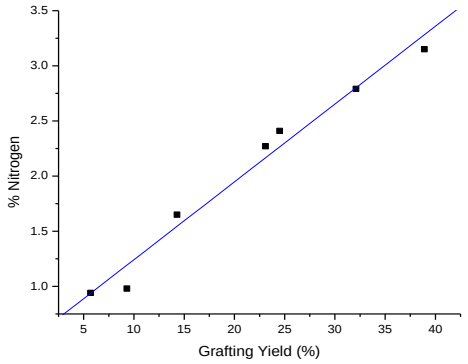

Fig.7. Elemental Analysis – Nitrogen content of various extend grafted cotton samples.

Scanning electron microscopy (SEM)

Grafting of MPTAC on cotton fibres evidently illustrated in SEM images which been shown in Fig. 9. It is clearly seen that the grafted fibres been coated with thin layers of MPTAC copolymer. The differences between virgin and grafted fibres are very mild and this might be due to the grafting percentage of tested fibres are quite low. Therefore, thick layer of copolymer coating could be visible at higher grafting yield.

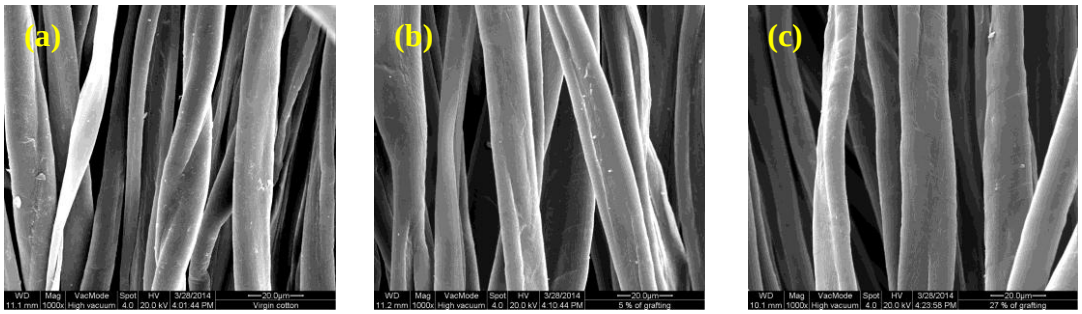

Fig.9. SEM images of 1) Control cotton 2) MPTAC-g-cotton (5% grafting) and 3) MPTAC-g-cotton (27% grafting).

Dye adsorption

Fig. 10 demonstrates the relation of dye adsorption capacity of MPTAC-grafted cotton with grafting yield. The adsorption capacity increases with grafting yield. The availability of active adsorption sites rises as the grafting yield increases. Hence, this site attracts more numbers of dye molecules (Kumar et al. 2012). The adsorption wasn't exactly increase linearly with grafting yield. The dye uptake capacity of cotton was relatively lower at higher grafting extent. Anyhow, the maximum dye uptake capacity of the grafted cotton sample was 150mg/g.

This may due to present of high density grafted chain at higher grafting extent which may obstruct the diffusion of bulk dye molecules from surface to core of grafted matrix. The dye uptake capacity was studied at varying concentration of dye solution with cotton with constant grafting yield.

Apart from that, the kinetic study for dye uptake by grafted cotton was performed as well. The saturation of dye adsorption was reached within 1 minute of reaction cycle. The results been shown in Fig.11. The dye uptake by grafted fibre with lower grafting yield was compatible enough adsorption of dye at concentration of 200ppm. This observation rationalize that the functional group of MPTAC is very efficient in dye uptake.

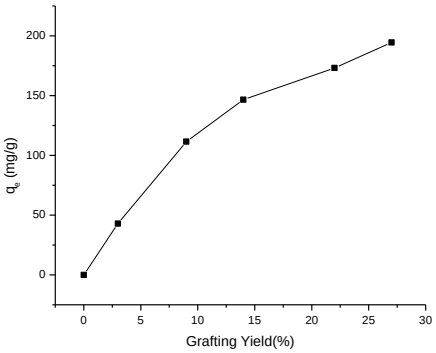

Fig.10. Adsorption of dyes on to MPTAC-g-cotton at different grating extent. [Dye] = 200ppm.

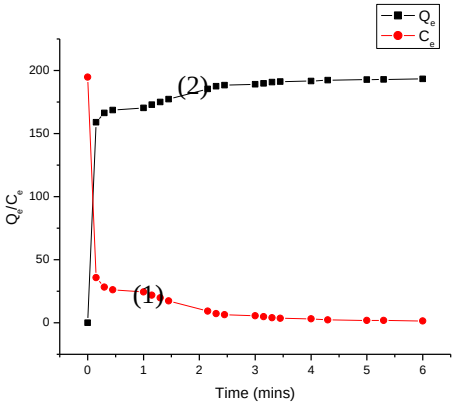

Fig.11. Adsorption equilibrium of grafted matrices versus time (G.Y. ~ 27%). [Dye] = 200ppm. 1) Q_e, 2) C_e .

Antimicrobial Analysis

Microbiological studies have been carried out for investigating the antibacterial and antifungal efficacy by qualitative and quantitative methods. Preliminary results indicated that Poly-MPTAC behaves to be bacteriostatic in nature. Qualitatively zone of inhibition was found 2mm (not very clear zone, brown halo up to 4 mm) for both *E.coli* and *S.aureus*. Quantitatively, grafted samples have been tested against *E.coli* and *S.aureus* by serial dilution and plating method. 20% grafted cotton was found to be 2 log cycle reductions for the tested bacteria. More detail studies are under progress.

CONCLUSION

Post irradiation grafting technique was successfully employed to graft quaternary ammonium group containing polymer Poly-MPTAC onto cotton fibre. Different grafting experimental parameters were studied to optimize the radiation induced grafting process in order to obtain desired grafting level. PMPTCA-g- cotton samples were tested for antibacterial activities and found to show antibacterial activity against gram positive and gram negative strains. Moreover, MPTAC grafted cotton were investigated for removal of textile dye from aqueous solution. The grafted cotton has potential to be used in textile wastewater treatment plants for dye uptake.

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