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Development and surface characterization of positively charged filters

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Filter media, which have been surface charge modified by modifiers with positive functional groups, are termed positively charged filters. The main aim of the present work was to manufacture positively charged filters for capturing negatively charged particles, mainly bacteria and virus from water. Filters were manufactured with varying ratios of base materials, processing conditions and charge modifiers. Experimental parameters were varied in order to attain filters with a high zeta potential to increase the filtration efficiency. A positive zeta potential of 42.56 mV has been attained with a charge modifier percentage of 100%, a stirring time of 30 minu., vacuum pressure of 15 cm Hg. Statistical analysis was performed to find the most significant parameter for positive charge modification.

1. Introduction

A filter is any porous material used to separate contaminant particles from a fluid. Filters are classified depending on the manner they separate particles in terms of pore structure and capture mechanism. There are two basic filtration mechanisms used to hold back particulates: (a) mechanical straining (b) electrokinetic capture. In mechanical straining, as the name implies a contaminant is separated from the solution by physical entrapment when the contaminant tries to pass through a pore smaller than itself. Whereas in the case of electrokinetic capture mechanism the particle or contaminant collides with the filter and is retained on the surface by attractive short range Van der Waal's forces [1]. The advantage of electrokinetic capture over mechanical straining is that the filter medium can separate very tiny particles, which are practically impossible to be separated by simple mechanical straining. Also, in electrokinetic capture, the pores need not be smaller than the particulates to retain them. The flow rates are higher making the process faster. Clogging of the medium with the particles is very less as the particles don't pass through the pores but get attached to the surface. Therefore the efficiency of the filter increases.

Membrane filtration with charged microporous filters is considered to be the best procedure to separate virus and bacteria from water. The advantage of a charge modified microporous membrane over a conventional membrane is the exclusion of particles on the basis of charge as well as size. Thus, for example, virus can be removed from a fluid without having to go to an ultrafiltration membrane [2]. Previously the filters used for virus removal from water were negatively charged at the pH of tap water (7 to 8). Most bacteria and virus are found to have a net negative charge at this pH value [10]. As a result, there was repulsion between the negatively charged filter surface and the negatively charged particles. The separation was thereby poor and required the treatment of the water with acids or salts to enable capture. But treatment of water could affect the particles and prove harmful to them. Therefore, filters with a positive charge are being used. These filters are manufactured by chemically binding positively charged molecules to the filter surface [4]. These molecules

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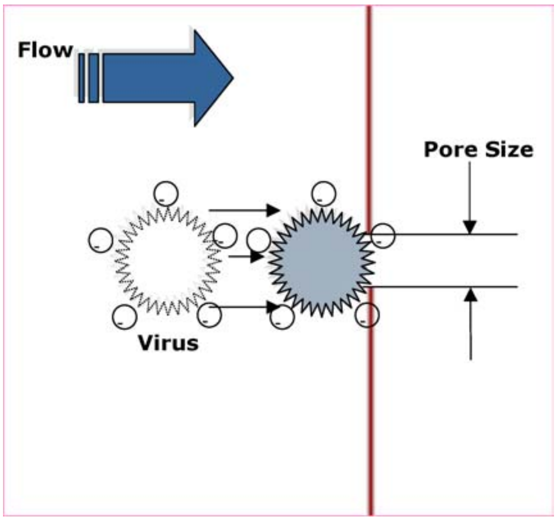


Figure 1 Conventional filter.

form electrokinetic capture sites for the separation of contaminants.

To summarize, positively charged filters have been found to have a substantiate advantage over the negatively charged filters as they can adsorb virus over a broader pH range and without the treatment of water with salts. The conventional and positively charged filters are shown in Figs 1 and 2 respectively to explain the mechanism. The present paper discusses the manufacturing process used for the positively charged filters by varying all processing conditions. The Figs 3 and 4 show the process and equipment used. Also a discussion on the effect of choice of charge modifier and base materials on the pore densities and zeta potential of the filters will be done.

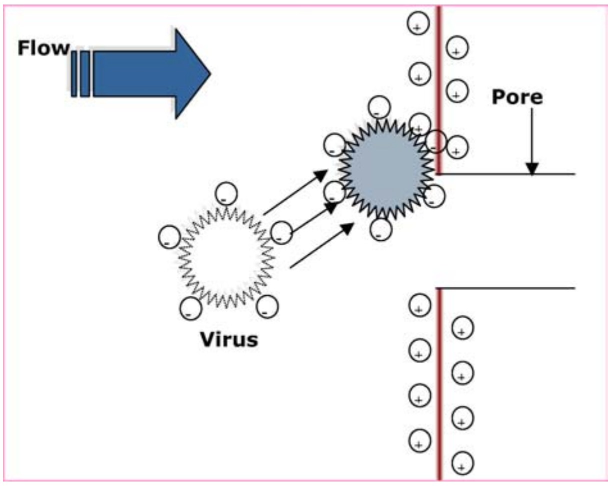


Figure 2 Positively charged filter.

2. Experimental

2.1. Materials

The base materials used were cellulose and glass fiber. Glass fiber was purchased from Johns Manville Company with a fiber diameter ranging from 0.2–0.75 μm. Cellulose was purchased from Donghae pulp. The cellulose chosen was Coho craft type with a fiber size of 20 μm. The charge modifiers A and B were used to impart the charge to the filter surface. Charge modifier A consists of colloid silica particles. The surface of the particles is coated with alumina. On mixing the charge modifier with water the alumina ionizes to give Al^{3+} ions. These cations then attach to the surface of the filter and render it positive. The structure of charge modifier A is shown in Fig. 5. From the TEM images in Fig. 6 it can be seen that the charge modifier is present as small particles and thereby easier for the modifier particles to adhere to the fibers to enable charge modification. The charge modifier B is used as coatings to make surfaces harder as well as in compounding some substances. The structure of this charge modifier is shown in Fig. 7. The two modifiers were studied to compare the charges they produced on the filters.

Water was used as the solvent for the two charge modifiers. PSL (polystyrene latex) particles of sizes varying from 0.2 to 2 μm were purchased from Duke Scientific Corporation. These latex particles are being used to test if the filters manufactured will be able to separate them. They serve as a good test example as most bacteria and viruses are also in the 0.2–2 micron range [4].

2.2. Manufacturing process

The base materials, glass fiber and cellulose were taken in desired proportions and mixed together to form a slurry. The type of processing used was wet processing. The charge modifier was dissolved in water to make a solution of desired concentration 10–70%. This charge

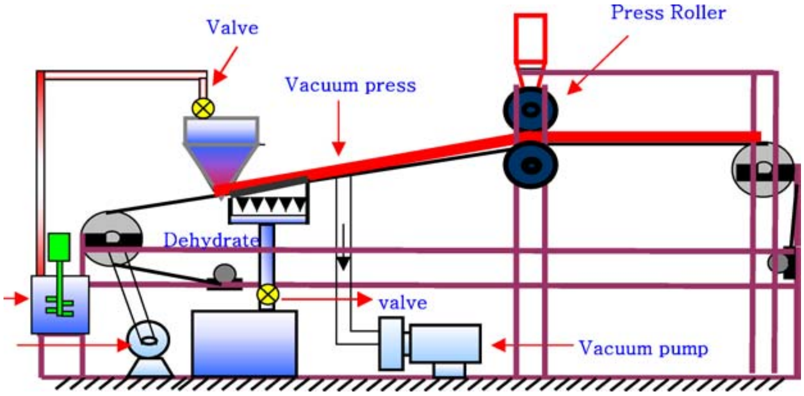


Figure 3 Schematic of manufacturing process.

Figure 4 Real time manufacturing process.

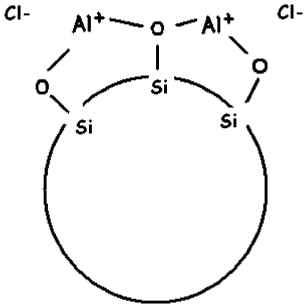


Figure 5 Structure of charge modifier A.

modifier solution was next mixed with the base materials solution. After agitating the mixture for some time the slurry was casted into long sheets. A vacuum pressure was applied to the sheets to remove excess water and enable good binding between filter and fiber. A roller pressure was applied to the sheet to densify the mixture, control the pore size and increase the mechanical strength of the filters. The sheet was subject to drying for some time for further removal of water and to allow time for thermosetting. Finally a dried filter, which has been, charge modified was obtained. The Fig. 3 shows the manufacturing process and the real time equipment used in the process is shown in Fig. 4.

2.3. Manufacturing conditions

After investigating the different kinds of charge modifiers, base materials and processing conditions used for the charge modification from literature survey, filters were made with different ratios of base materials (0:100 to 100:0 glass fiber: cellulose) and different charge modifier percentages (10, 20, 40 and 70%). The drying time was varied from 1 min to 6 h and vacuum pressures of 50 cm Hg and 15 cm Hg were employed. A constant pressure force of 6 kgf/cm^2 and a drying temperature of 130°C were used. In each case the pore size and zeta potential of the manufactured filters were measured. The pore size was measured with the help of an Autopore III 9420 porosimeter and cross checked by SEM (Scanning Electron microscopy) images with image processing softwares such as GAIA Blue and Scion Imaging. The Tables IA, B, IIA and B show the filters manufactured for the two charge modifiers with varying processing conditions. The zeta potential or charge of the filters was measured with an Otsuka ELS - 8000 zeta meter. The present paper discusses the effect of the choice of charge modifier, base material ratios and percentage of charge modifier on the parameters zeta potential and pore size of the filters.

2.4. Electron microscopy analysis

Scanning electron microscope (SEM) images were obtained using an AMRAY 1400 microscope. A small piece of the filter was cut from the sheet and placed on a sample stub. The filter was then lightly coated with platinum-palladium wire and imaged with SEM to obtain charge modifier distribution on fibers.

3. Results and discussion

3.1. Effect of pore size on virus adsorption

The pore size of the filter media is defined as the average diameter of a single pore in a membrane. The performance of a membrane depends vastly on the pore size ratings. As the pore size is reduced, membranes are used for micro and ultrafiltration to remove very

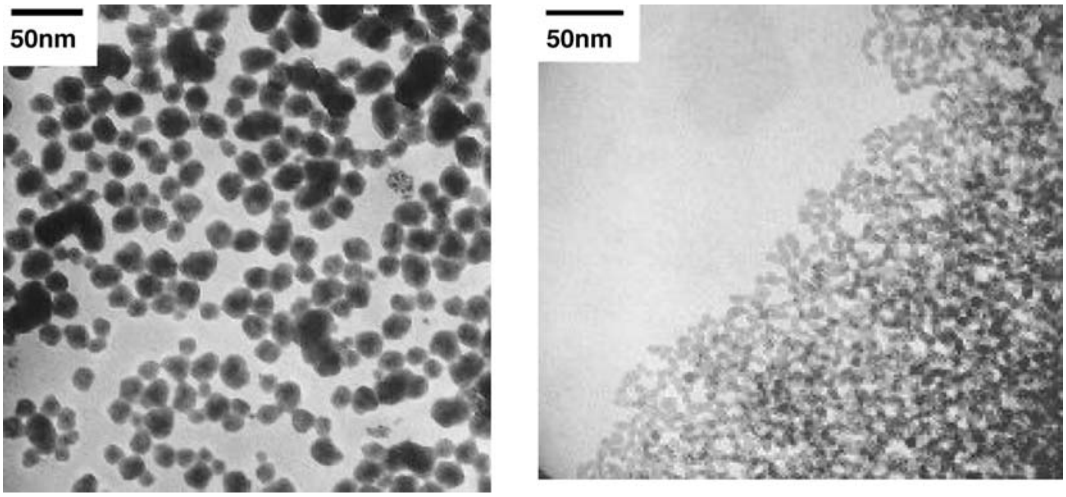


Figure 6 TEM images of charge modifier A.

TABLE IA Manufacturing conditions with charge modifier B

	Glass fiber	Cellulose	Charge modifier B	Vacuum pressure	Roller pressure	Stirring time
12-1	75%	25%	10%	50	6	1
12-2	75%	25%	20%	50	6	1
12-3	75%	25%	40%	50	6	1
12-4	50%	50%	10%	50	6	1
12-5	50%	50%	20%	50	6	1
12-6	50%	50%	40%	50	6	1
13-1	75%	25%	10%	20	6	1
13-2	75%	25%	30%	20	6	1
13-3	50%	50%	10%	20	6	1

TABLE IB Manufacturing conditions with charge modifier B

	Glass fiber	Cellulose	Charge modifier B	Vacuum pressure	Roller pressure	Stirring time
14-1	10%	90%	10%	50	6	1
14-2	25%	75%	10%	50	6	1
14-3	50%	50%	10%	50	6	1
14-4	75%	25%	10%	50	6	1
14-5	90%	10%	10%	50	6	1
15-1	50%	50%	10%	50	6	1
15-2	50%	50%	20%	50	6	1
15-3	50%	50%	30%	50	6	1
15-4	50%	50%	40%	50	6	1
15-5	50%	50%	70%	50	6	1

TABLE IIA Manufacturing conditions with charge modifier A

	Glass fiber	Cellulose	Charge modifier A	Vacuum pressure	Stirring time
18-1	0%	100%	50%	50	6 hr
18-2	25%	75%	50%	50	6 hr
18-3	50%	50%	50%	50	6 hr
18-4	75%	25%	50%	50	6 hr
18-5	100%	0%	50%	50	6 hr
20-1	50%	50%	50%	50	1 min
20-2	50%	50%	50%	50	5 min
20-3	50%	50%	50%	50	10 min
20-4	50%	50%	50%	50	30 min
20-5	50%	50%	50%	50	60 min

TABLE IIB Manufacturing conditions with charge modifier A

	Glass fiber	Cellulose	Charge modifier A	Vacuum pressure	Stirring time
22-1	50%	50%	30%	50	30 min
22-2	50%	50%	50%	50	30 min
22-3	50%	50%	70%	50	30 min
22-4	50%	50%	100%	50	30 min
22-5	50%	50%	200%	50	30 min
22-6	50%	50%	500%	50	30 min

small particles from the fluid not even visible to the naked eye. However there is no absolute method to determine the pore size of a membrane. In the present work, pore size has been measured by image processing with GAIA Blue software and with an Autopore III 9420 porosimeter. There are some standard tests to measure the pore size. One such example is the bubble point test. The bubble point test however, cannot be used for hydrophobic membranes. The filtration permeabilities depend on the pore size, which in turn depends on the filtration media. The filter media used for the manufacture of charged filters in our work is a mixture of cellulose and glass fibers. Cellulose is a naturally occurring high molecular weight glucose polymer with a crystalline structure. Majority of the membranes are made with cellulose. The main cause for using cellulose is that it forms a self-bonding matrix for the membrane. Glass microfibers were used as the second base material.

Fibrous materials with a large surface area are known to be examples of good filter media. These materials are characterized by small fiber diameter in the micron to sub-micron range and are generally referred to as microfibers. Glass fiber is one example where the fibers are a fraction of micron to several microns. As a result, glass fiber was used as the second base material in the manufacturing process. The Fig. 8 shows the SEM micrographs of filters manufactured with different ratios of base materials. These filters were manufactured with a pressure force of 6 kgf/cm^2, a vacuum pressure of 50 cm Hg, and a drying temperature of 133°C for 25 min. Charge modifier A was used for positive charge modification. The Table III shows the variation of pore sizes for filters manufactured with different ratios of base materials and different percentages of charge modifiers used.

Since most bacteria have sizes ranging from 0.02 to 2 μm and the goal of the work was to manufacture filters to trap such bacteria a pore size of 0.3 μm was tried to be attained by varying the base materials ratio. A size of 0.3 μm was chosen because too small pore sizes would create problems of clogging and reduction in flow rates making the filtration process very slow and too high pore sizes would let the bacteria to pass through. From the Table III it was found that for glass fiber: cellulose ratios of 50:50 we were able to achieve the desired pore size of 0.3 μm. This ratio was thereby optimized and used for the

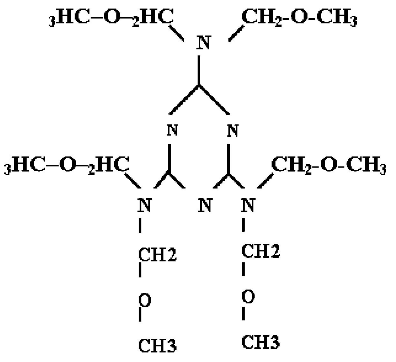


Figure 7 Structure of charge modifier B.

TABLE III Variation of pore size with base material ratio and charge modifier percentage

	Glass fiber: Cellulose	Pore sizes (μm)	Charge modifier%	Pore sizes (μm)
1	0:100		10	0.36
2	25:75	0.25	20	0.25
3	50:50	0.3	30	0.28
4	75:25	0.22	40	0.3
5	100:0	0.24	70	0.26

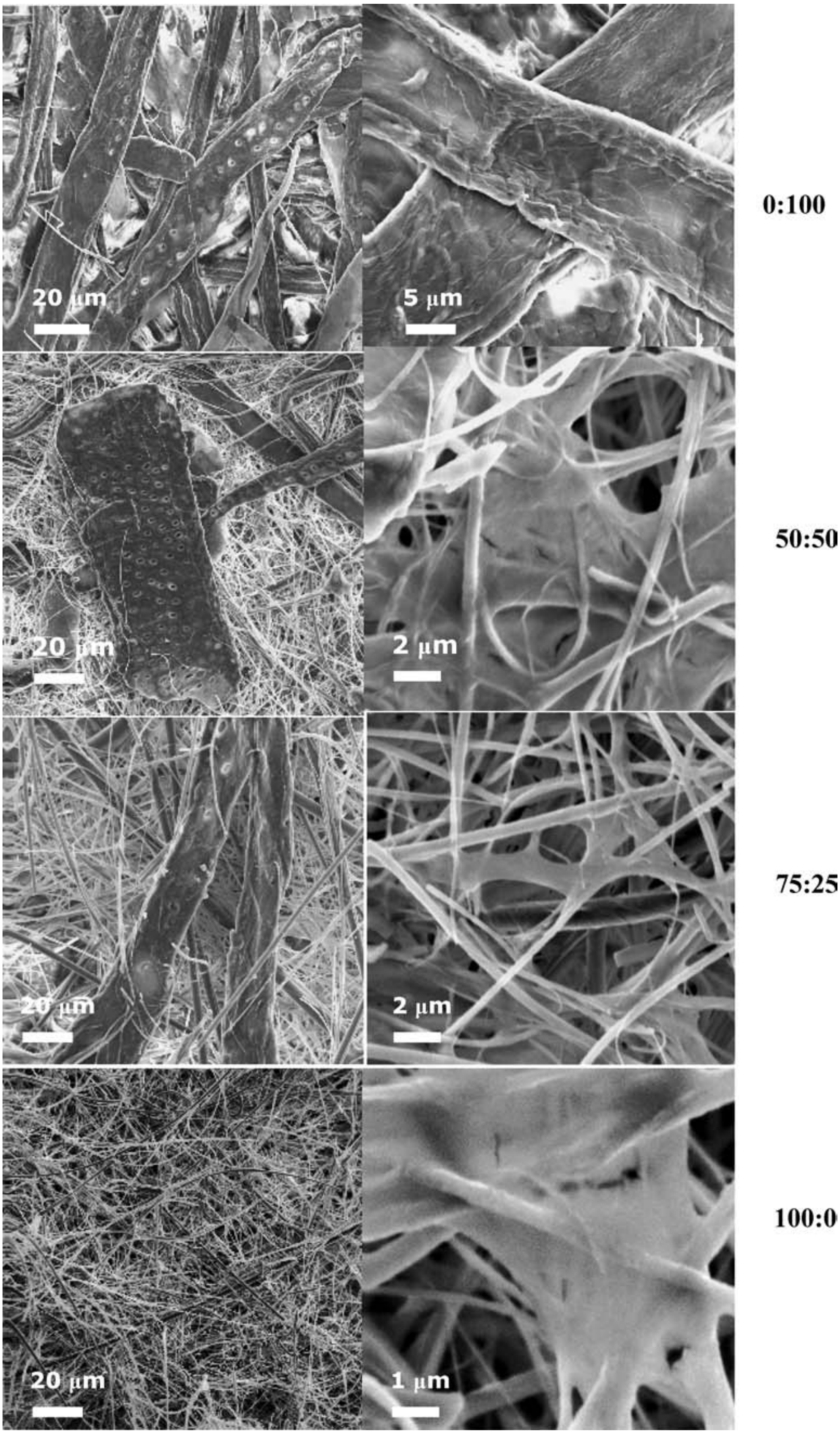


Figure 8 SEM micrographs of filters manufactured with different ratios of glass fiber: cellulose.

further manufacture of filters. However with the increase of charge modifier percentage it is found that there is a decrease in the pore size. This can be obviously explained that as the amount of charge modifier increases, more the coverage on the fibers and the total void area decreases, reducing the pore size. That is why there is a decrease of pore size from 0.36 to 0.26 μm as the charge modifier percentage increases from 10% to 70%. The SEM images in Figs 9 and 10 show the filters manufactured at varying charge modifier percentages of charge modifiers A and B respectively. It can be inferred from the images that the coverage of

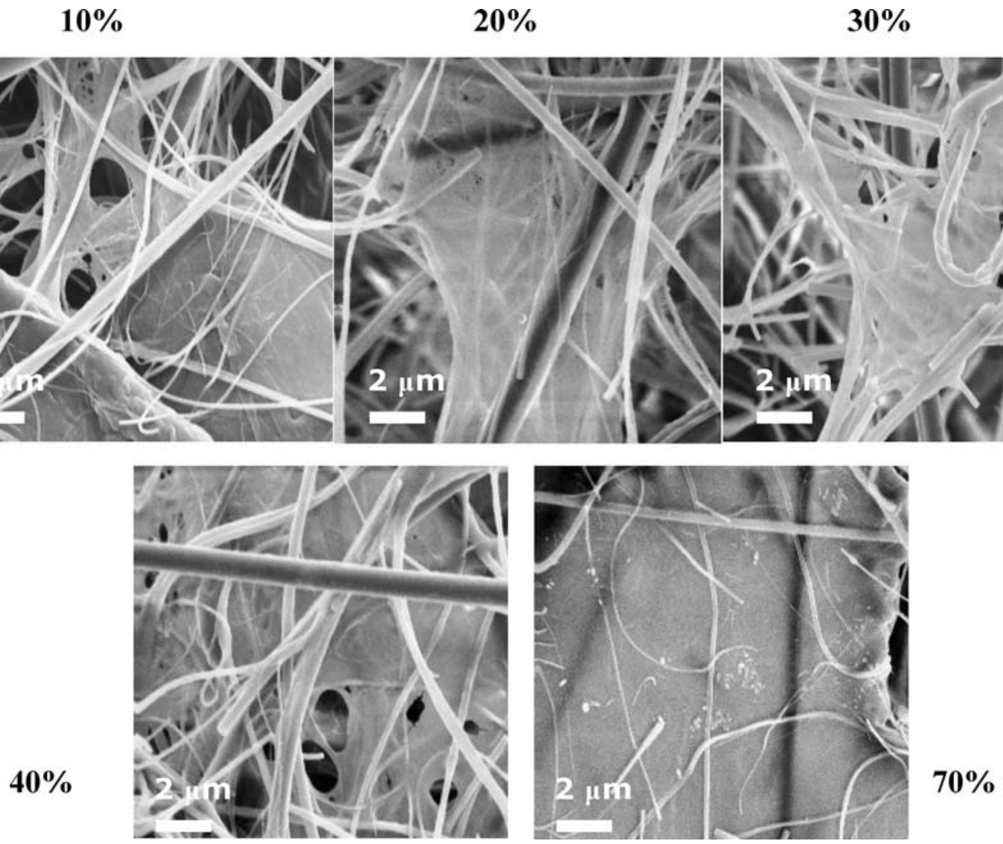


Figure 9 SEM Micrographs of filters manufactured with varying percentages of charge modifier A.

charge modifier on the fibers is better with the charge modifier A.

3.1.1. *Measurement of pore size*

The pore sizes were measured with the help of software called GAIA Blue to cross check the values obtained from the porosimeter. If we consider the pore to be of circular nature, then the diameter of the circle would essentially be the pore size of the pores. Three points were marked on the edges of the pores as shown in Fig. 11 and the software is used to draw a best fit circle passing through the three points. The software then gives the values of the diameter, which is the pore size. About 15 pores were marked on each image and about 5 images were image processed to get the average pore size.

3.2. Effect of surface zeta potential on virus adsorption

The surface charge can be measured in terms of the zeta potential. The zeta potential exhibited by the filter surface depends on the material used for the manufacture of the filter. But the zeta potential can be varied by binding other materials to the filter. In the eletrokinetic capture mechanism separation takes place when the suspended particles come in contact with the filter surface. If the surface is positively charged it can attract negatively charged particles and vice versa. But in order for such a contact to take place the zeta potential of either the particle to be separated or that of the filter surface must be equal to zero. On the other hand, the zeta potentials of the filter surface and the particle to be separated can be of opposite nature.

The goal of the present work was to manufacture filters with very high zeta potential values. First, the zeta potentials of the base materials and the filters manufactured were found with the help of an Otsuka ELS −8000 zeta meter. It was found that glass fiber had a zeta potential of −37.5 mV. Cellulose was found to have a value of −39 mV; charge modifier B had zeta potential of −17.23 mV and charge modifier A had 19 mV. Charge modifier A was the only one, which had a positive zeta potential.

The Table IV shows the values of zeta potentials obtained for the two charge modifiers on varying the ratio of base materials. Since charge modifier A had a positive zeta potential it was expected that the filters manufactured out of them should have a positive zeta potential too. On the contrary, the filters exhibited a negative zeta potential as shown in Table IV. These filters were manufactured with a stirring time of 6 h, vacuum pressure of 50 cm Hg. However the charge modifier percentages used were 10% charge modifier

TABLE IV Variation of zeta potential with ratio of base materials

	Glassfiber : Cellulose	ZP (mV) Charge modifier B	ZP (mV) Charge modifier A
1	0:100	−15.19	−28.07
2	25:75	−18.57	−32.13
3	50:50	−24.10	−39.25
4	75:25	−36.89	−35.96
5	100:0	−47.27	−30.47

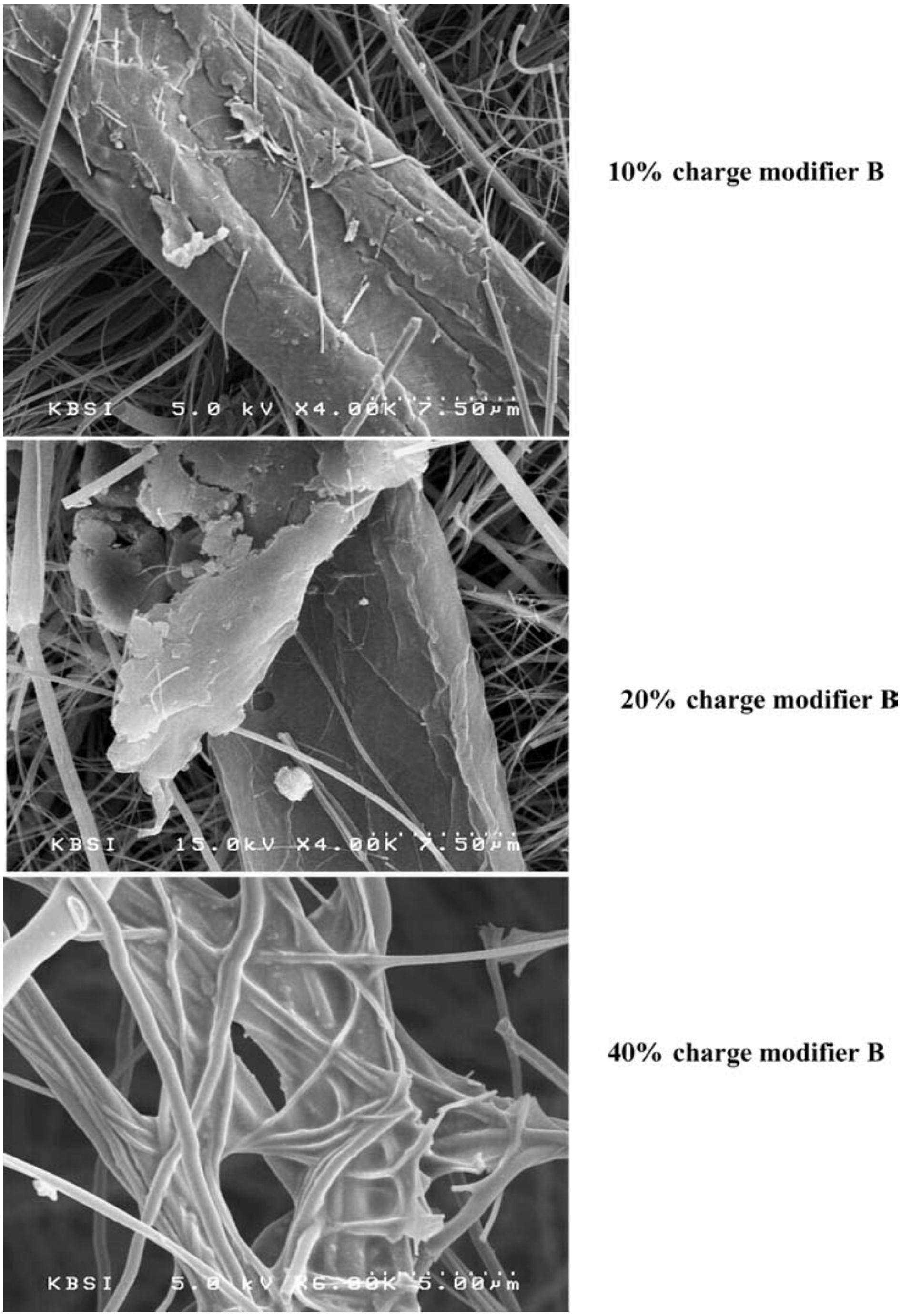


Figure 10 Filters manufactured with varying percentages of charge modifier B.

B and 50% charge modifier A. It is therefore concluded that 50% charge modifier A was not sufficient to obtain a positive zeta potential. Next filters were manufactured by increasing the percentage of charge modifier A from 50%. The two charge modifiers were initially chosen to compare which of the two could generate charged filters. When the charge modifier A was increased to 100% and the vacuum pressure reduced to 15 cm Hg, it was found that the filters exhibited a positive zeta potential for all values of base material ratios. A very high percentage of charge modifier can enable better adhesion and distribution of the charge modifier on the fibers. A lower vacuum pressure enables a larger amount of the charge modifier to remain on the filter surface thereby increasing the zeta potential. These could be the reasons for the charge shift from negative to positive. The Table V shows the positive values produced.

TABLE V Variation of zeta potential with ratio of base materials by increasing charge modifier percentage

	Glass fiber: cellulose	ZP (mV)
1	0:100	27.47
2	25:75	36.58
3	50:50	37.92
4	75:25	42.56
5	100:0	39.48

Now, since we know that charge modifier A can be used for manufacture of positively charged filters, we next investigated the effect of varying charge modifier

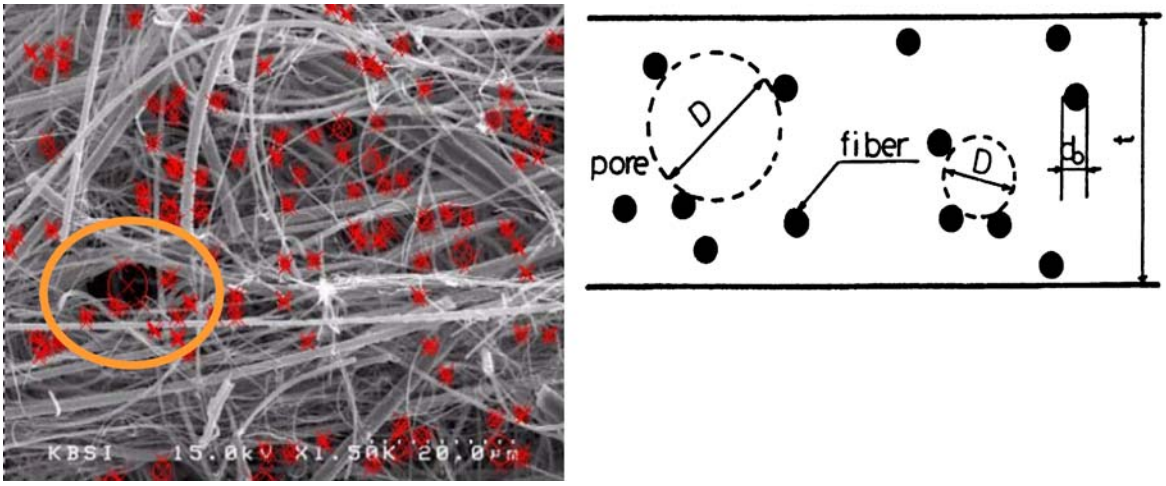


Figure 11 Image analysis to find pore sizes.

TABLE VI Variation of zeta potential with charge modifier percentage and choice of charge modifier.

	Charge modifier%	Zeta potential (mV) Charge modifier B	ZP (mV) Charge modifier A
1	10	−27.42	−16.59
2	20	−24.75	−12.53
3	30	−18.58	31.13
4	40	−18.36	46.55
5	70	−16.42	31.43

percentages on the zeta potential. It can be observed from the Table VI that the filters manufactured with 10 and 20% of charge modifier A imparted only a negative charge to the filter surface and are not sufficient for the charge modification. But 30, 40 and 70% charge modifiers gave zeta potentials of +30 mV, 46.5 and 31.43 mV respectively. Thus, at least a minimum of 30% charge modifier was essential to reach positive zeta potential. These filters were manufactured with a vacuum pressure of 50 cm Hg, roller pressure of 6 kgf/cm^2 and a ratio of cellulose: glass fiber = 50:50.

However the charge modifier B gave filters with negative zeta potentials irrespective of the amount of charge modifier employed. It is therefore demonstrated that charge modifier A is a better choice for positive charge modification over charge modifier B.

3.3. Effect of stirring times on charge modification

The present work uses two charge modifiers A and B to reduce the negative charge on the filter surfaces to enable electrokinetic capture of finely suspended particles. The charge modifier particles adhere to the surface of the filter material and produce highly charged sites. The effect of stirring time was studied to observe the variation of zeta potential with time. Two times, 30 min and 6 h were used with 50:50 ratio of glass fiber: cellulose, a vacuum pressure of 50 cm Hg with charge modifier. The charge modifier was varied from 30, 50 and 70%. It can be seen from the Table VI that higher zeta potentials were obtained with a higher stirring time of 6 h. For example with 70% charge modifier and a stirring time of 30 min, a negative zeta potential of 21.16 mV was obtained. But the filter with 6 h stirring time and all other parameters constant gave a positive zeta potential of 31.43 mV. The time of stirring or agitation does seem to have a large effect on the charge modification process as seen from the SEM micrographs in Fig. 12 and zeta potential values from Table VII.

TABLE VII Variation of zeta potential with stirring time

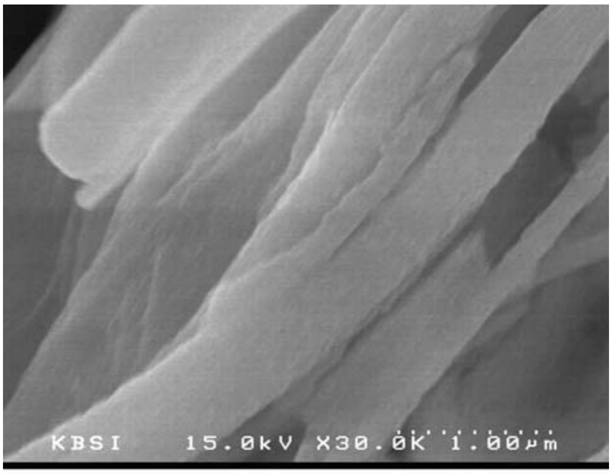
Charge modifier A	ZP at 30 min stirring time	ZP at 6 hrs stirring time
30%	−43.14	31.13
50%	−34.75	21.93
70%	−21.16	31.43

The reason is that charge modifier A is very sparingly soluble in water. As discussed earlier we are trying to make filters by dispersing the charge modifier on the fibers by dissolving in water. As the charge modifier is sparingly soluble in water, the time of stirring plays a significant role in dissolving more amount of charge modifier in the water and ionize to form the ions, which would basically be responsible for the charge modification. According to the basic ionization equation

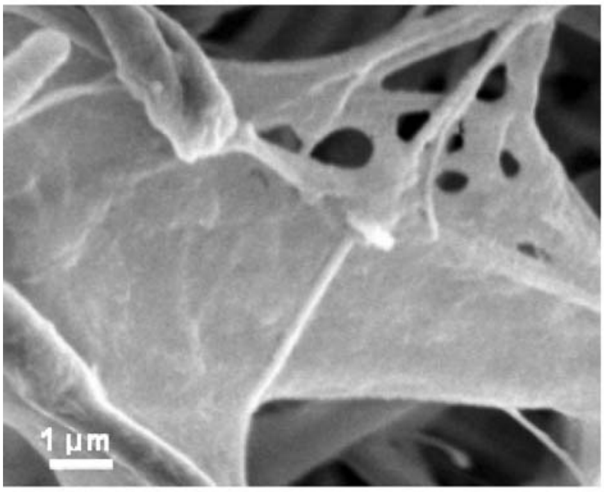
The ionization constant is given by $K = [A^+][B^-]/[AB]$

Here $[A^+]$ and $[B^-]$ are the concentrations of the product and $[AB]$ is the concentration of the reactant. The ions $[A^+]$ and $[B^-]$ formed will vary depending on the time taken for the dissolution of AB in water. More the time of reaction, more number of ions will be formed. Since in our case we are concerned with cations, more number of cations will be formed. These will then attach to the filter surface and create positive capture sites. Therefore the agitation time of the charge modifier in water plays the most prominent role in rendering the charge of the filter surface positive.

But since it is an equilibrium reaction the concentration of ions formed will reach a maximum and then remain constant. In the present work since we have found that the positive charge has increased by increasing



Stirring Time = 6 hours



Stirring time = 30 Minutes

Figure 12 Effect of stirring time on charge modifier coverage.

stirring time, we could be working in the increasing part of the graph. Based on the same theory, charge modifier B is also sparingly soluble in water, but positively charged filters could not be made from it as it demonstrated negative zeta potentials.

4. Conclusions

It is concluded that charge modifier A is a better charge modifier than charge modifier B for positive surface charge modification of filters. At least 30% charge modifier A was required to attain a positive zeta potential, with 50:50 ratios of glass fiber and cellulose. But a 30% of charge modifier B gave a negative zeta potential. Filters with a pore size of 0.3 μm could be manufactured which can trap most bacteria. Finally a filter with a high positive zeta potential of 42.56 mV was able to be obtained with 100% of charge modifier A, at 75:25 ratio of glass fiber: cellulose, stirring time of 30 min and vacuum pressure of 15 cm Hg.

Acknowledgments

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