



Comparison of nanodiamond coated quartz filter with commercial electropositive filters: Zeta potential and dye retention study

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ABSTRACT

Diamond coated quartz(DQ) electropositive filters were compared with a few commercially available electropositive filters. The zeta potential of all the filters were measured and it was found that DQ had higher positive zeta potential over a wide pH range. Dye retention tests, using acid black II dye, performed on all the filters showed DQ to have higher retention. The study clearly showed that, under laboratory conditions, DQ has better performance compared to many commercial electropositive filters.

1. Introduction

Clean water access for all is one of the major challenges of the 21st century, faced by all governments across the planet in varying degrees. In 1990 only 76% of world population had access to sustainable safe drinking water [1,2]. This was increased to 91% under the Target 7C of the Millennium Development Goals (MDGs) by 2015 [1,2]. This essentially means as of today at least 700 million people have no access to clean and safe drinking water. The major factors contributing to clean water shortages are, population growth and industrialisation. Some of the major contaminants in water, making it unsafe for consumption are bacteria, viruses, metals, industrial products etc [3–8]. The present state-of-the-art for removal of these contaminants involve nanofiltration (NF) [9,10] or reverse osmosis (RO) [11,12]. However, both these techniques suffer from variety of drawbacks limiting their usages to central water treatment facilities [9,11,13–16].

Adsorptive depth filtration (ADF) has emerged as a major alternative to RO and NF requiring lower pressure differential and less to no power input. Unlike NF/RO, where size exclusion is the primary technique, filtration in ADF is achieved through attractive forces like van der Waals, electrostatic or hydrophobic interaction [17]. This makes it possible to design ADF filters with high flow rates under low pressure. Also, for nanoscale contaminants mechanical filtration is ineffective and ADF is the most appropriate technique [18]. For ADF filters to work effectively it is important that the long-range electrostatic forces are put to good use. Unlike van der Waals forces, which are short range and always

attractive, electrostatic forces can be both attractive or repulsive depending on the surface charge of the filter material. Traditional filter materials like, quartz, glass, cellulose etc have negatively charged surface in water making them unsuitable for most contaminants which are also negatively charged [19–24]. To overcome this drawback, various types of coatings have been applied to filter media surfaces to make them electropositive. Some recent examples of such coatings are alumina [25], magnesia [26,27], yttria [24,28–30], zirconia [31,32], copper oxide [33,34], iron oxide [35–37], metallic salts [38,39] and poly electrolytes [40–43]. Even though such electropositive coatings show improved adhesion of contaminants to filter elements, the coatings themselves are prone to poor adhesion to membrane support, low zeta potential, low isoelectric point etc. to name a few. The high positive charge in any electropositive filter improves the filtration in two ways, first, higher charge means higher retention capacity and second, the higher charge results in longer interaction length thus allowing higher flow rates through the filter media. The effect of the lower zeta potential was also observed in this study where most commercial filters had low positive zeta potential, this required longer interaction time with the contaminant which was facilitated by the low flow rates through the filter. Due to the lower flow rates of commercial filters the filters had to be tested using a dipping method rather than by passing the contaminated water through the media, as has been discussed below.

In an earlier study by Bland et al. [44], the methodology and effectiveness of diamond coated quartz filter has been demonstrated. The main focus of this work is to compare the effectiveness of the diamond

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coated quartz filter against a few commercially available electropositive filters. The zeta potential of all filters as a function pH has been measured. The Brunauer–Emmett–Teller (BET) surface area of each filter were also measured. The dye adsorption/retention of a fixed volume of each filter was estimated for comparison with diamond coated filter using acid black II dye.

2. Methods and materials

2.1. Filters

In this work diamond coated quartz filters (DQ) have been compared with five commercially available electropositive filters. The DQ filters were prepared by loading diamond nanoparticles on to binderless quartz filter made from quartz fibres. The quartz fibres were obtained from Millipore. The full details for making these filters have been described elsewhere [44]. The commercial filters are, 3M-Zetaplus (ZP), Invitrogen - Brightstar (BS), ErtelAlsop - Zeta-pak (ZK), Pall - Posidyne (PS) and Argonide - Nanoceram (NC). Amongst them ZP and ZK are cellulose based filters, BS and PS are nylon based and NC is a filter based on combination of glass and alumina. ZP, ZK, PS and NC filter media were taken from the commercially available filter cartridges. BS filter paper was purchased from Thermofisher for this study. The filters were imaged using a Hitachi SU8200 series scanning electron microscope (SEM) operating at 2 kV and a working distance between 11 and 16 mm.

The manufacturers description of various commercial filters are listed below. The wordings have been taken from manufacturers website or technical documents released by the same. ZP is depth filter composed of Zeta Plus SP Series depth filtration media, inorganic filter aid, cellulose and a resin system. The media in ZK is composed of cellulose, DE or Perlite, and wet strength resin. PS filter cartridges have a patented covalent charge-modified Nylon 6,6 membrane which exhibits a net positively-charged Zeta potential in aqueous solutions. BS is described as a filter composed of porous, nylon 66 matrix, derivatized with quaternary ammonium groups and finally NC is thermally bonded blend of microglass fibres & cellulose infused with nanoalumina fibres in a non-woven matrix creating an electropositively charged depth filter media.

2.2. Zeta potential measurements

On immersing a solid into a liquid, the solid surface acquires a surface charge. The surface charge attracts ion from the liquid media which become tightly bound to the solid surface. Since the surface of the solid is charged it generates a potential which decreases with distance from the solid surface. The potential at the interface between liquid and tightly bound ions is known as zeta potential. In case of the filters the solid surfaces are stationary. In this configuration if an electrolyte is forced through the filter then ions attached to the solid surface will experience a shearing force and will start moving along with the electrolyte. Moving ions will create a potential which can be measured by placing electrodes on opposite sides of the channel and was first suggested by Wagenen et al. [45]. By measuring the potential/current as a function of electrolyte pressure it is possible to measure the zeta potential using the Helmholtz- Smoluchowski equation [46].

One of the first difference between DQ and the rest of the filters is permeability. While DQ is highly permeable and allows large fluid flow rates at nominal pressure, the commercially available filters require much higher pressures for fluid flow. In the earlier work on DQ [44], the zeta potential as well as its retention properties were measured by directly passing fluids through the filter. However, in the present study due to low permeability of the commercial filters, a different approach was adopted. The zeta potential of all the filters were measured using SurpassTM 3 electrokinetic analyzer which can be used to measure zeta potential of variety of materials of different shapes and sizes [44,47,48]. The SurpassTM 3 calculates the zeta potential by measuring the change in

streaming potential with electrolyte pressure across a streaming channel using two Ag/AgCl electrode placed either side of the channel. For the present study, the filters were shredded into narrow strips as shown in Fig. 1. Panel A in the figure shows the shredded BS filters in deionised (DI) water. Panel B and C in the same figure shows DQ and ZK filters respectively. The filter pieces were repeatedly washed with DI water to get rid of any particulates from the filter formed as a result of shredding process. The cleaned filters were then mounted across the streaming channel in SurpassTM 3. A 10^{-3} M solution of KCl was used as electrolyte. The electrolyte pressure was varied between 200 and 600 mBar. 0.1 M HCl and 0.1 M NaOH was used to vary the pH of the electrolyte with the inbuilt titrator in SurpassTM 3.

2.3. Dye retention

The dye retention study was done by dipping a specified volume of filter media in a dye solution as opposed to passing the solution through the filter media [44]. This was due to the low permeability of the commercial filter requiring long duration for filtering small volumes of solution at ambient pressures. The dye solution was made by dissolving acid black II in water. The final concentration of the dye in water was 40 mg/l. To keep the volume of each media same a home made setup, as shown in Fig. 2, was used to measure the media volume. The setup consists of a brass tube with 14 mm inner diameter. Two plastic perforated ends were used to hold the media in place while pressure was applied on the filter media with a fixed torque screw driver (0.5Nm) and brass rod. The media were cut into small pieces as shown in Fig. 1. They were first soaked in DI water. The pre-soaked media was then mounted inside the apparatus shown in Fig. 2. For the present study, a compressed volume of 0.3 cm^3 was taken for each filter. The selected volume was then introduced in small vials containing 25 ml of dye solution. The absorbance of the solutions were measured using a UV-vis Spectrophotometer GENESYS 10S at the absorbance maximum of acid black II at 575 nm. The shredded filters were left in the solution for approximately 24 h. To calculate the dye retention the absorbance of the solutions were measured before introduction of filters and then measured again after the filter pieces have been left in the solution for 24 h. The retention percentage was calculated as $R(\%) = \frac{Abs_m - Abs_t}{Abs_m} \times 100(\%)$ [44] where Abs_m is the absorbance of master solution and Abs_t is the absorbance of solution after filter media has been left in for 24 h.

2.4. Surface area analysis

The surface area of all the filters were measured using BET technique. The BET specific area of the filters were measured using Quantachrome QuadraSorb-evo. The samples were degassed at 200°C for 3 h before the measurements. The results of the BET study is tabulated in Table 1. The densities of the filters are also listed in the same table. The densities were calculated by weighing the compressed filters used in the dye retention study. The compressed volume of the weighed filters were used for calculation purposes.

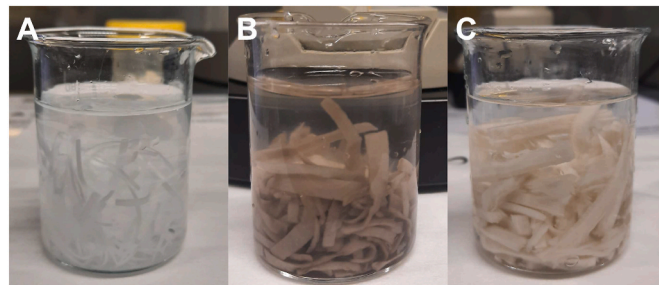


Fig. 1. Shredded filters in water for zeta potential measurement. A) Birgthstar, B) Diamond coated quartz, C) Zeta-pak



Fig. 2. Setup for making equal volumes of filter media.

Table 1

The BET surface area of all the filters are tabulated here. The mass density of the filters are tabulated in column three. The densities were calculated by measuring the weight of the filters used in the dye retention study.

Filter type	BET surface area (m ² /g)	Density (g/cm ³)
Diamond coated quartz	30.3	0.52
3M – Zetaplus	14.0	0.50
Invitrogen - Brightstar	26.0	0.45
ErtelAlsop - Zetapak	4.2	0.50
Pall - Posidyne	17.2	0.46
Argonide - Nanoceram	19.9	0.53

3. Results and discussion

Fig. 3 shows the SEM images of the filters used in this study. Panels A and B show the images for cellulose based filters ZP and ZK. The fibrous nature of the filters are clearly visible in the images. It is also clear that fibres in both these filters have been pressed together to create a 3D mesh which works as a depth filter. In contrast, PS and BS are essentially membrane filters. Panels C and D show the images of the nylon based filters, PS and BS, respectively. As stated before, these filters are markedly different from the cellulose based filters. These filters consist of small pore like structures. The images in panels C and D are split into two parts. The right hand side shows the close up of the filters showing the micro/nano pores in the filter media. These filters are best used for separating charged contaminants from liquid after larger particles have been filtered out. Due to its membranous nature these are also likely to be more susceptible to fouling. Panel E shows the image of the NC filter surface. The NC filter is slightly different from the others that have been tested here. The schematic of the NC filter is shown in panel F of Fig. 3. The positive filter media in case of NC is encapsulated between two support layers [25]. This is essentially a depth based on glass and alumina. Finally, panel G shows the diamond coated quartz filter. The fibrous and highly porous nature of the filter is clearly visible in the image. DQ is also a depth filter, thus allowing higher flow rates while filtering out smallest of the particles like acid black II dye.

The zeta potential of various filters as a function of pH is shown in Fig. 4. The cellulose based filters (ZP and ZK) have isoelectric point close to pH 6. This makes the filters ineffective for many viruses whose isoelectric points are greater than or equal to 6 [23]. Both filter media show a zeta potential of \sim -20 mV under high pH conditions. The NC filter shows positive zeta potential across the whole range of measurements. The filter could be measured only between 5 and 10 pH values as that is the manufacturer specified effective pH range. This puts it at some disadvantage when compared with other filters in terms of pH range of operation. The nylon based filters (PS and BS) also show positive zeta potential over the whole range of measurement. The zeta potentials of BS, PS and NC vary between 30 mV and 5 mV for low and high pH respectively. The DQ filter in comparison have much higher positive zeta potential over the whole pH range of measurement. It varies between 52 mV and 35 mV for low and high pH respectively. This makes DQ a very

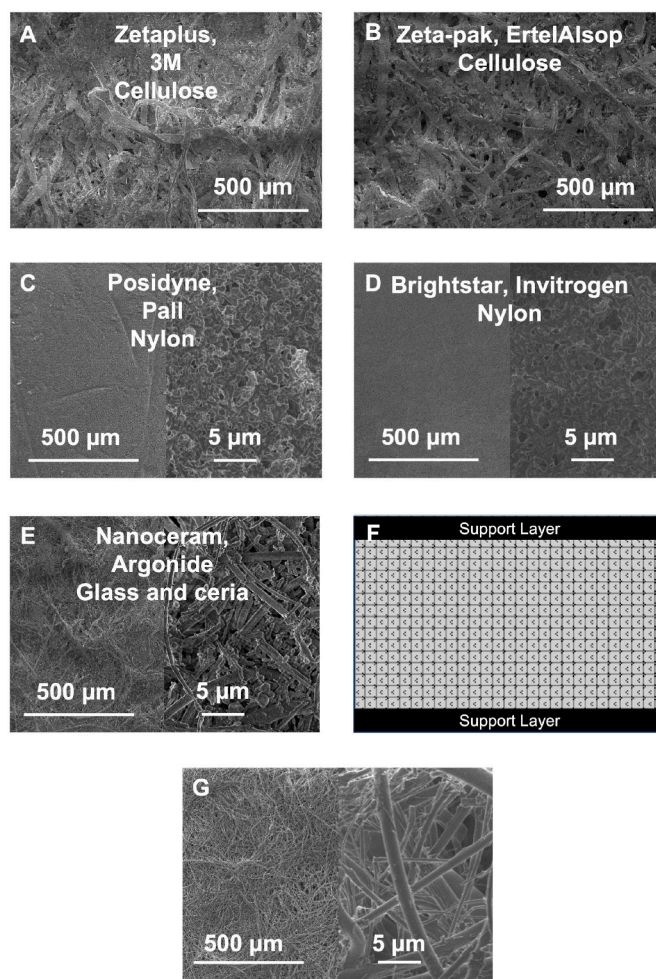


Fig. 3. SEM images of the commercial filters used in this study is shown in this figure. Panels A and B represent the images for cellulose based filters. Panels C and D show the SEM images of the nylon filters. Panel E shows the alumina based Nanoceram filter. Panel F shows the schematic of the Nanoceram filter showing the filter media encapsulated between two support layers. Panel G shows the diamond coated quartz filter used in this study.

effective filter media for capturing/filtering the whole range of viruses shown in Michen et al. [23].

The zeta potential of the material is directly related to the surface charge of the material. Low zeta potential means that the surface charge density of the material is also low. As a result the point up to which the surface is effective in capturing particles of opposite charge is closer to the surface. The direct consequence of this is seen in the design of the filters using electrokinetic effects for filtration. Low surface charge means a longer time is needed for interaction between the filter media and the colloid/solution for effective filtration. This means that the flow rates through the said media have to be purposefully kept low to have more effective filtration. Keeping this in mind and looking at the zeta potential data, it is clear that DQ would be able to handle much larger flow rates for efficient filtering action. To test the retention efficiency of the filters, the filters were dipped in acid black II solutions and the retention was measured using the methods described before.

Fig. 5 shows the dye retention (black squares) of various filters after the filters have been left in the acid black II solution for 24 h. The blue solid circles in the same figure shows the total surface area of the filters used for the study. The red triangles show the zeta potential of the filters at pH 8.37. The left y-axis shows the retention percentage, the right y-axis (red) shows the zeta potential and the extreme right y-axis (blue) shows the total area. The zeta potential has been lifted from Fig. 4 by

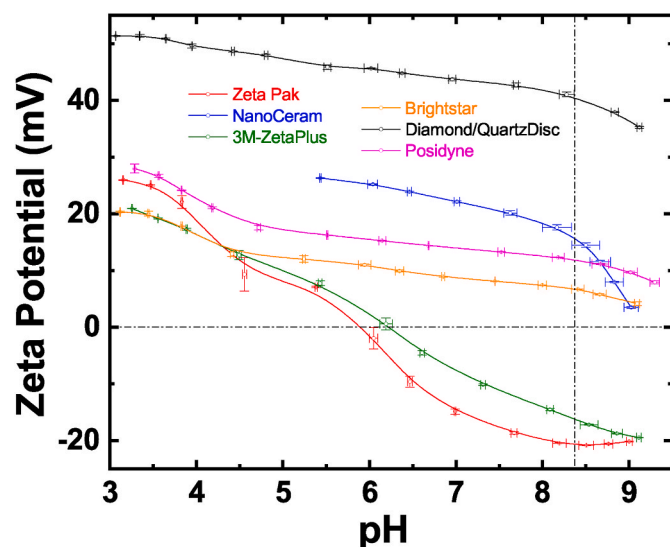


Fig. 4. Zeta potential as a function of pH for the various commercial filters and their comparison with diamond coated quartz filter. The dotted line shows the pH value at which dye retention study was carried out.

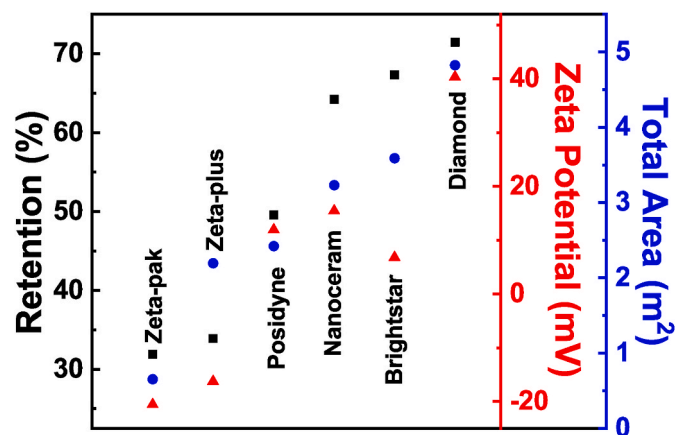


Fig. 5. Dye retention of various filters after being soaked in acid black II solutions for 24 h shown in black squares. The red triangles show the zeta potential of the filters at pH 8.37. The blue dots show the total surface area of the filters used in the experiment. The left axis shows the retention percentage, right y axis (in red) shows the zeta potential and the extreme right y-axis (in blue) show surface area. The three sets of data are labeled for the filters they represent.

interpolating the zeta potential vs pH data. The total surface areas shown in Fig. 5 were calculated using the BET and density data from Table 1. The data set is mainly meant to show dye retention trend between the various filters and hence no error bars have been shown.

The pH of the dye solution was measured to be ~ 8.37 . This is indicated by a vertical dashed line in Fig. 4. Based on the data presented in Fig. 5, the increasing order of zeta-potential from negative to positive is $ZK < ZP < BS < PS < NC < DQ$ at pH ~ 8.37 . However, the data on retention follows a slightly different order. The order in this case is $ZK < ZP < PS < NC < BS < DQ$, with DQ showing 71% and ZK showing 32% retention. So, to pin the retention solely on zeta potential may not be fully appropriate. A consideration should also be given to the total surface area available for each filter media for a given volume (since the retention was done keeping the volumes constant).

The results from such a study should also be taken carefully, since most of these filters are complex filters consisting of many components and the total area of the electropositive components will be difficult to

determine. Secondly, the retention was calculated based on the filters being dipped in the dye solution. So, as the solution becomes lighter with absorption of the dye, the rate of absorption will also go down since less and less dye is available for absorption, and that will also effect the retention results for high absorbing filter media like DQ and BS. An alternative protocol that can be adopted for this experiment is to pass the same volume of dye solution through same volume of filter media and calculate retention and time taken for the solution to pass as measure of efficacy of the filters. Given the low permeability of the commercial filters this experiment will have to be done under considerable applied pressure to pass measured volume of liquid in reasonable time scales. This approach was not taken in this work due to lack of experimental setup. Nonetheless, the dip approach presented in this work gives a clear indication of the effectiveness of each filter in removing acid black II dye from the solution.

4. Conclusion

In conclusion we have compared diamond coated quartz filters (DQ) with various commercial electropositive filters. DQ was found to be more electropositive than all the commercial filters over the whole range of pH measurements. The BET surface area of DQ is larger than other filters. The BET area of the DQ filters used in this study was $30.302 \text{ m}^2/\text{gm}$. However, this is not the saturation value for such filters. In the earlier study [44] the maximum surface area achieved was $88 \text{ m}^2/\text{gm}$. DQ filters also showed the highest retention for acid black II dye under similar test conditions. To conclude, within the comparison protocol used in this study, DQ was found to be a better electropositive filter than most commercial filters.

CRediT authorship contribution statement

Soumen Mandal: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Project administration, Funding acquisition. **Greg Shaw:** Investigation, Resources, Writing – review & editing. **Oliver A. Williams:** Conceptualization, Methodology, Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. URL <https://linkinghub.elsevier.com/retrieve/pii/S0065216408700546>.

Data availability

Data will be made available on request.

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