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STUDY ON WETTABILITY OF RADIATION-INDUCED GRAFTED INDUSTRIAL POLYETHYLENE (PE) FILTER CARTRIDGE FOR WATER CONTAMINANT ADSORPTION

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ABSTRACT

Synthetic polymeric materials are making their way into water treatment and being utilized due to easy tailoring in promising end applications. Industrial Polyethylene (PE) filter cartridge is a type of water filter cartridge with 100% polyethylene material with superior chemical compatibility and particle retention efficiency for use in a wide range of applications such as industrial water treatment, drinking water treatment, sterilization, gas processing solvent, vent filter, and gas filtration. Radiation-induced grafting technique is one of the most popular methods for polymeric materials surface modification. In this study, an industrial polyethylene filter cartridge was modified via a simultaneous radiation-induced grafting process by employing gamma irradiation at 25 kGy. The Glycidyl Methacrylate (GMA) was grafted onto the material which was followed by subsequent chemical functionalization with an amine functional group. This modification improves the hydrophilic properties of the material as an adsorbent. The amine functionalization was confirmed by FTIR spectroscopy analysis. The unmodified and modified filter cartridges have been subjected to contact angle measurements using the advanced mode contact angle method through an optical contact angle (OCA). This analysis identified changes in material hydrophilicity. According to the results, the modified filter cartridge is more hydrophilic than the unmodified cartridge. A filter cartridge with enhanced hydrophilicity is suitable for the removal of various types of contaminants, including metal ions, dye particles, pathogens, fertilizers and pharmaceutical residues from water.

Keywords: Radiation induced grafting; Industrial PE filter cartridge; Gamma irradiation; Chemical functionalization; Optical contact angle

INTRODUCTION

Industrialization and economic growth, especially in developing countries, have led to enormous water pollution. This is mainly due to the release of highly toxic and harmful metal ions into water bodies. Addressing the growing emphasis on water pollution and remediation, extensive research has been conducted on the removal of metal ions from water. In particular, this can be accomplished through the modification of polymeric materials. Two prominent factors need to be considered in the modification of polymeric materials, first, the selection of polymeric materials and second is the technique used for modification.

Eco-efficiency is considered a major criterion in the selection of polymers for metal removal from water, whereby the materials should be economical in terms of cost and also promising of an easy and continuous supply (Kumar et al., 2019). Recently, a number of researchers have focused on the usage of cellulosic biofibers or biopolymers due to their abundancy, biodegradability, and hydrophilicity nature (Kolya & Kang, 2023; Kumar et al., 2019; Abinder et al., 2016; Madrid et al., 2013). Abinder et al., (2016) report that these biofibers have several advantages, but also some limitations, including poor mechanical properties and brittleness at room temperature, as well as sensitivity to moisture. Therefore, alternatively, the development of economically viable fabricated polymeric materials for metal ions removal is strongly anticipated.

Synthetic polymeric materials hold advantages over bio-based polymers in terms of mechanical and chemical properties. Moreover, synthetic polymeric materials offer higher flexibility in their physical forms and are also prone to chemical modification for the attachment of various functional groups that cater to the end application (Chalykh et al., 2023; Barsbay et al., 2016; Kavakli et al., 2016). In this study, industrial polyethylene (PE) filter cartridges are subjected to surface modification to improve the properties for the removal of metal ions from water selectively. Practically, industrial polyethylene (PE) filter cartridges is extremely hydrophobic and widely used in water filtration system. But unfortunately, it is incapable of removing some contaminants, especially metal ions. The current industrial PE filter cartridge function based on the size exclusion which is purely physical with involving any chemical interaction (Lombardo & Brigano, 2014). Therefore, this type of filtration system is superficial, compromising and inefficient. The water is contaminated with heavy metals and dyes resulting in major health complications such as the risk of cancer, neuronal damage, diabetes, and cardiovascular disorders (Rehman et al., 2018).

In general, there are several surface modification techniques to enhance polymeric materials' surface properties, including surface coating, surface functionalization, and surface grafting (Mozetič, 2019). The main aim of the modification is to improve and introduce a specific characteristic that acts as a precursor for metal removal from water. Among these modification techniques, graft polymerization is one of the most familiar methods to overcome polymers' shortcomings. Moreover, based on Nor Fadzil et al., (2020) graft polymerization is more stable due to the interaction of covalent bonds by incorporating a monomer onto the porous membrane surface. Despite this, graft copolymerization of a monomer onto surface material by gamma, UV, or electron beam provides an effective approach for incorporating advantageous modification of the surface properties to form active sites for grafting without affecting the basic properties of the polymeric backbone (Artico et al., 2023; Mozetič, 2019; Shin et al., 2017; Barsbay and Güven, 2013; Thakur et al., 2012). According to Shin et al., (2017) radiation-induced grafting polymerization (RIGP) presents unique advantages over other grafting methods due to its simplicity, homogeneous reaction, control over the process, and the absence of initiators and catalysts for polymerization. Hence, this method is an effective approach to improving functional properties by increasing the adsorbent's wetting properties. Basically, the technique involves incorporating a monomer on the surface and functionalization of the grafted polymer chains with known functional groups (Artico et al., 2023; Barsbay and Güven, 2013).

Wettability is the term used for hydrophilicity, while hydrophobicity describes the relative affinity of water molecules to spread on the surface of any substrate (Junchou et al., 2020). In principle, synthetic polymeric materials such as polyethylene, polypropylene, polyvinyl chloride, and nylon possess poor wettability. This is one of the major disadvantages of water-based adsorbents. Thus, synthetic polymeric materials require further improvement for the effective removal of metal ions from water. Generally, radiation-induced grafting and amine functionalization processes could amend the wettability properties of polymeric materials. As a result, evaluating the hydrophilicity behavior of the adsorbent after surface modification processes is critical. The wettability properties description of the materials could be conducted via contact angle measurement. This will give valuable information regarding its hydrophobicity and hydrophilicity.

This study focuses on the modification of an industrial polyethylene (PE) filter cartridge via gamma irradiation and a simultaneous radiation-induced grafting technique in which glycidyl methacrylate (GMA) was grafted onto the material and then chemically functionalized with various types of amine. Both unmodified and modified filter cartridges have been thoroughly characterized for their degree of surface hydrophilicity using the advanced mode contact angle method via an optical contact angle (OCA). This study provided insight into the wettability evaluation of the adsorbent by contact angle measurement. It demonstrated the success and the impact of the radiation-induced grafting technique and the amine functionalization process.

EXPERIMENTAL

The industrial source provided was an industrial PE filter cartridge (PENSONIC 0.5 microns). Glycidyl Methacrylate Acid (GMA, ≥90%, Sigma Aldrich), Polysorbate 20 (Tween-20, ≥40%, Sigma Aldrich), Ethylene Diamine (EDA, ≥99%, acros), Dimethyl Amine (DMA, <50%, Sigma Aldrich), Isopropyl Alcohol (IPA, 70%, QRëC) and Methanol (≥99.8%, Friendemann Schmidt) were used in this study in their original grade. Distilled water was used to rinse the grafted material. The chemical structure of EDA and DMA are shown in Figure 1.

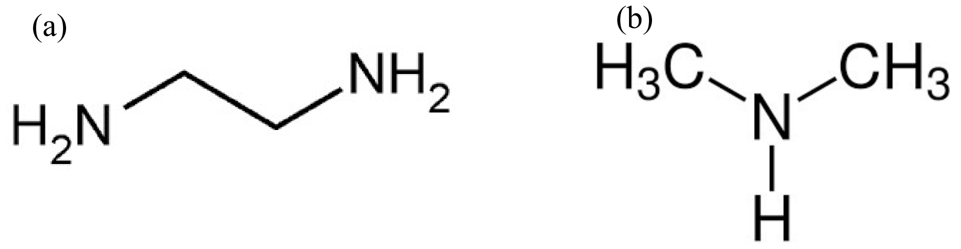

Figure 1. Chemical structure of (a) EDA and (b) DMA

Simultaneous Radiation Induced Grafting of Industrial PE Filter Cartridge

An emulsion solution composed of GMA at different concentrations (5, 7, and 10% w/w) and Tween-20 (1 wt%) was prepared, followed by de-oxygenation for 15 minutes with N_2 bubbling.

The pre-treated PE cartridge was immersed in the grafting solution and the mixture was de-oxygenated again for another 10 minutes and prolonged immersion in the grafting solution at room temperature for 24 hours. The samples were irradiated with ^{60}Co gamma rays at the SINAGAMA facility. The irradiation was performed at a dose of 25 kGy. An accredited ceric-cerous and ferrous sulfate (Fricke) dosimetry system, which is in compliance with MS ISO/IEC 17025 standards, was used to determine the amount of absorbed dose. Finally, the un-reacted monomer and homopolymers were removed by rinsing with methanol and distilled water.

The samples were dried in a vacuum oven at 60 °C for 24 hours until a constant weight was reached. The grafted filter cartridge was weighed to determine the degree of grafting (DG) using the following Equation (1):

$$DG(\%) = \frac{Wf - Wo}{W_o} \ x \ 100 \qquad (1)$$

Where, W_f and W_O are the weight of grafted and original industrial PE filter cartridges respectively (Othman et al., 2019).

Chemical Functionalization of Grafted Industrial PE Filter Cartridge

The grafted industrial PE filter cartridge was chemically functionalized using two types of amine groups EDA and (DMA. Both amine solutions were prepared with 70 wt% and 30 wt% of an IPA.

The grafted sample was immersed in an amine solution and reacted in a water bath at 70°C for 1 hour. The chemically modified PE filter cartridge was washed in methanol and distilled water. Finally, the sample was dried in a drying oven at 60 °C for 24 hours until a constant weight was reached. The functionalized industrial PE filter cartridge was weighed to find out the amine group density (AGD) using the following Equation (2):

$$AGD\ (mmol/g) = \left[\frac{(\frac{Wf - Wo}{W_o})}{MW}\right] x \ 1000 \qquad (2)$$

Where W_f and W_O are the weight of functionalized and grafted industrial PE cartridges respectively and MW is molecular weight for amine group (Othman et al., 2019).

Fourier Transform Infrared Spectroscopy (FTIR)

The analysis of filter cartridges before and after modification were characterized by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) using a Bruker Tensor II FTIR spectrometer. The FTIR spectra were recorded by an OPUS software spectrum by transmittance with 16 numbers of scanning at a resolution of 4 cm^{-1} with a wavelength range of 4000 – 500 cm^{-1} at ambient condition.

Wetting- Surface Characterization of Industrial PE Filter Cartridge

The raw, grafted, and functionalized industrial PE filter cartridges were measured using an Attention Theta (Biolin Scientific, Finland) interfaced with a PC for control and data acquisition. Two techniques were applied for the assessment, sessile drop goniometry and sessile drop goniometry with surface topography.

Optical Contact Angle Measurement

The most common technique used for surface wetting characterization is sessile drop goniometry due to its simplicity. The samples were held vertically to the sample stage during the measurement. The contact angles were obtained by positioning the tip that contains deionized water near the sample surface. The tip squeezes water at a constant drop liquid volume of 7µL. The contact angle measurement was completed within 10s. The measurement of contact angles for raw, grafted, and functionalized industrial PE filter cartridges was analyzed using the Young equation. This assumes that the material surface is chemically homogeneous and topographically smooth (ideal surface).

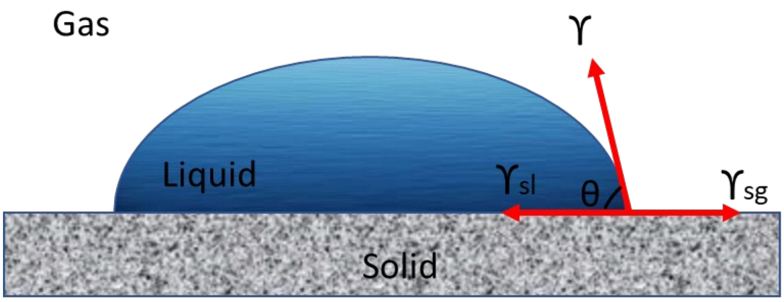

Figure 2. A contact angle on ideal solid surface determined by Young Laplace equation's

Figure 2 shown the droplet on the ideal surface which the Young's equation was applied (Huhtamaki et al., 2018; Young, 1805) and measured the reading of the contact angle as in Equation (3) (Huhtamaki et al., 2018):

$$\cos\theta_{Young} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma} \quad (3)$$

Where θ_{Young} is the Young contact angle, γ is the surface tension of the liquid, γ_{sv} and γ_{sl} are solid-vapor and solid-liquid interfacial tensions respectively.

Optical Contact Angle with Topography Measurement

The same measurement was applied to sessile drop goniometry with surface topography. The sample stage contained deionized water and the liquid volume was set up at 7μL depositing the surface material. Before the liquid was dropped on the surface material, the sample was subjected to topography to calculate surface roughness.

The morphology and roughness of the raw grafted with 7% GMA and functionalized industrial PE filter cartridges were measured over a relatively flat surface for practical measurement using optical contact angle with topography. The measurement area for each surface sample was fixed within 1.4 mm x 1.1 mm five times of repeated scanning. The root mean square roughness value was used as the evaluation index to analyze the difference in surface morphology and roughness among raw, grafted, and functionalized materials.

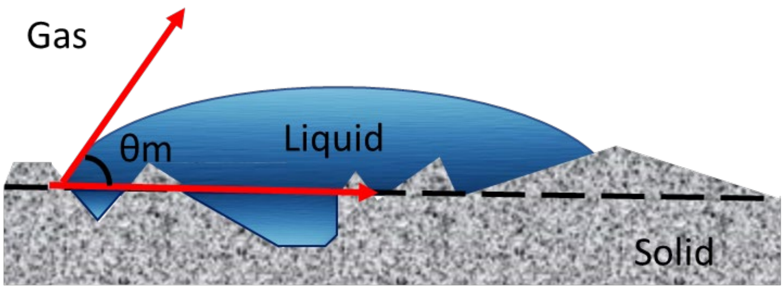

Figure 3. A contact angle on an actual surface material with inherent roughness

The droplet on the actual surface of the material is illustrated as in Figure 3 (Biolin Scientific, 2017). Based on the figure the measurement of contact angle calculated by considered the real surface which the Wenzel statement was applied as in Equation (4) (Wenzel, 1936):

$$\cos\theta_m = r\ \cos\theta_y \qquad (4)$$

Where, θ_m is the measured contact angle, r is the roughness ratio and θ_y is the Young contact angle.

Roughness ratio, r is defined as the ratio between the actual and projected surface areas which r is equal to 1 for a smooth surface and greater than 1 for a rough surface. The r for Wenzel equation is determined from the 3D area factor, S_{dr} based on the following Equation (5) (Biolin Scientific, 2017; Peltonen et al, 2004):

$$r = 1 + \frac{Sdr}{100} \qquad (5)$$

RESULTS AND DISCUSSION

Modification of the Irradiated Industrial PE Filter Cartridge

The effect of GMA concentrations of 5%, 7%, and 10% on the grafting yield of the industrial filter cartridge was examined. The results obtained are shown in Fig. 4. The simultaneous irradiation technique at a dose of 25 kGy with a reaction time of 24 hours was used for this investigation. The grafting yield increased as the concentration increased to about 10%. However, at monomer concentrations greater than 7%, the formation of homopolymers may also contribute to increased grafting yield. According to Nasef and Sugiarmawan, (2010) grafting yield increased with a GMA concentration of up to 10%. The concentration of GMA above 10% lead to the decreasing in grafting yield thereafter due to the fast-initial reaction rate. This was expected because the monomer was exposed to gamma irradiation. Thus, for practical reasons, GMA concentrations were limited to 5% and 7% w/w.

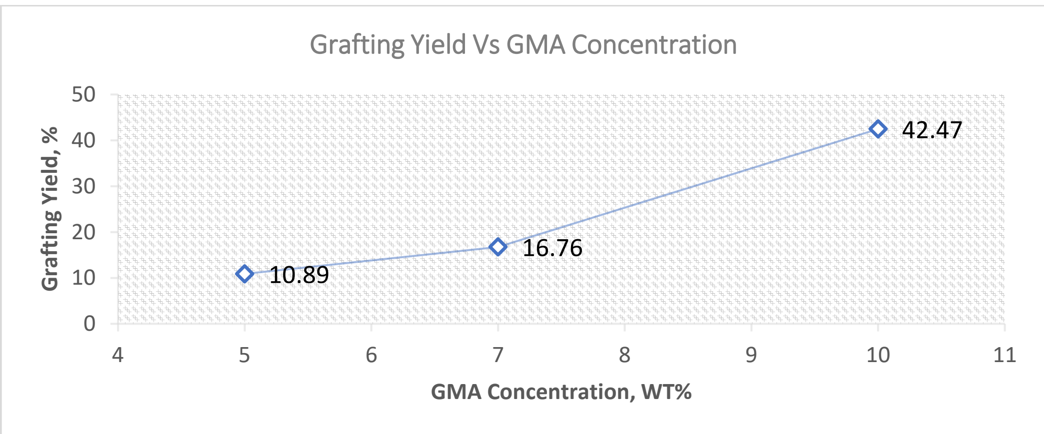

Figure 4. The grafting yield obtained as a function of GMA concentration for irradiated industrial filter cartridge

The amount of functionalized DMA and EDA expressed as AGD was determined gravimetrically. The effect of GMA concentration on AGD is shown in Fig. 5. As expected, the AGD demonstrated an ascending pattern for 5% and 7 % of GMA concentration and insignificantly reduced at 10% of GMA concentration. The EDA density increases from 0.87 mmol/g to 1.29 mmol/g as the GMA concentration increased up to 7%. Similar trends were observed for DMA as well but the AGD was slightly lower than EDA. A higher amine density was observed on the grafted adsorbent when the number of amines was greater (Liu et al., 2010). However, as the concentration of GMA was 10%, the density of EDA was reduced to 0.25 mmol/g. This phenomenon was due to the creation of a homopolymer in which the surface of the adsorbent was fully covered with branched grafted chains of GMA (Desmet et al., 2011) and the possibility of the chain collapsing led to amine attachment failure. Therefore, the highest AGD for an effective adsorbent could be achieved by using the largest number of amine groups, EDA.

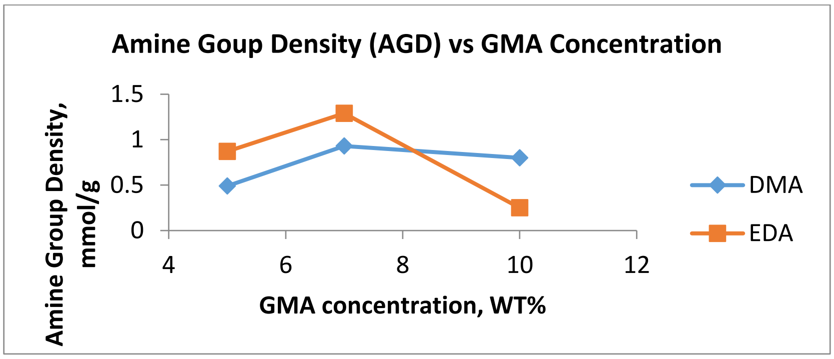

Figure 5. Effect of different GMA concentration on amine group density at 70 ^{0}C for 1h, 70% Amine: 30% IPA

FTIR Analysis

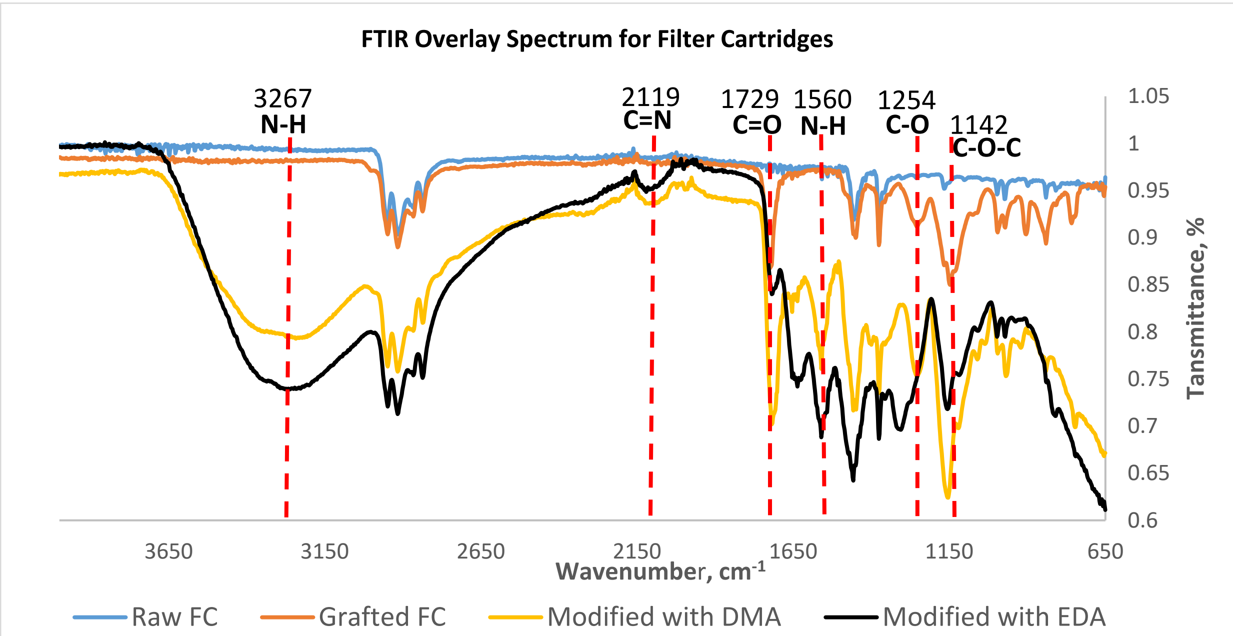

Figure 6. FTIR Spectra of raw, grafted at 7% of GMA concertation and functionalized with DMA and EDA

The FTIR analysis was performed on GMA-grafted material and subsequent chemical functionalization with an amine functional group to enhance its hydrophilicity as an adsorbent. FTIR analysis was used to characterize the surface composition of filter cartridges before and after modification. Figure 6 shows the IR spectra of raw, grafted, and modified filter cartridges. After grafting the filter cartridge with 7% GMA, the spectra exhibited distinct peaks indicating successful grafting interactions. These peaks are carbonyl group (C=O) at 1729 cm^{-1}, ester group C–O, and C-O-C vibration which originates from –COO– ester group of GMA at 1254 cm^{-1} and 1242 cm^{-1}, respectively (Abudonia et al., 2018). In addition, the characteristics of transmittance peaks arising from aliphatic amine groups are also identified. Specifically, the peaks at 3267 cm^{-1} correspond to N-H stretching, whereas the peaks at 2119 cm^{-1} and 1560 cm^{-1} represent the C=N group and N-H bending respectively (Rania, 2023). In addition, these peaks further verify the success of the radiation-induced grafting technique used to modify the sample.

Water Contact Angle Analysis

The water contact angle on the surface of raw, grafted, and functionalized industrial PE filter cartridges based on GMA concentration was measured. The results are exhibited in Fig.7(a)-(c). The raw industrial filter cartridge displayed a higher contact angle since PE is hydrophobic in nature. However, based on Fig.7(b), modified industrial PE filter cartridges showed a significant reduction in contact angle at 7% of GMA concentration. The contact angle reduced from 139º to 133.57º after grafting, and then to 122.53º and 114.11º after functionalization, respectively. This is due to the existence of polar functional groups such as carbonyl (C=O) in GMA and amine (NH_2) in DMA and EDA (Hebbar et al., 2017). As a polar group, carbonyls have a partially charged ion. The negative charge of the oxygen atom may interact with water molecules to form hydrogen bonds and become more hydrophilic. Similarly, the amine group is also negatively charged and capable of H-bonding, which supports polar hydrophilic groups.

Furthermore, EDA contact angle values are much lower than DMA due to the presence of two NH_2 molecules attached to the hydrocarbon chain. Hence, the changes in wetting properties of the raw filter cartridge can be correlated with functional groups attached to the surface. This is due to the simultaneous irradiation grafting technique. The contact angle measurement is also influenced by the material surface roughness.

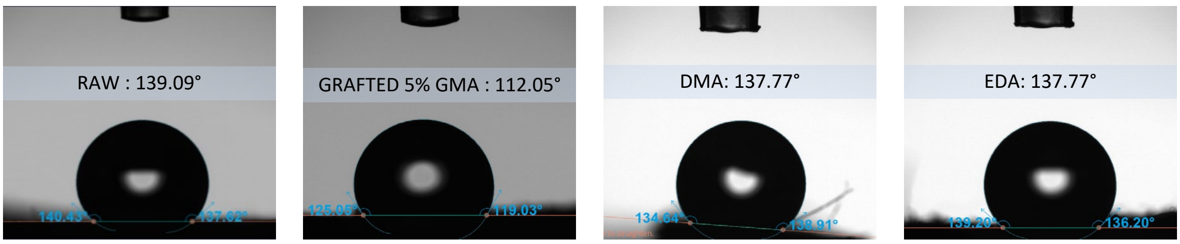

Figure 7(a). Contact angle for raw, grafted and modified industrial PE filter cartridge with 5 wt% of GMA

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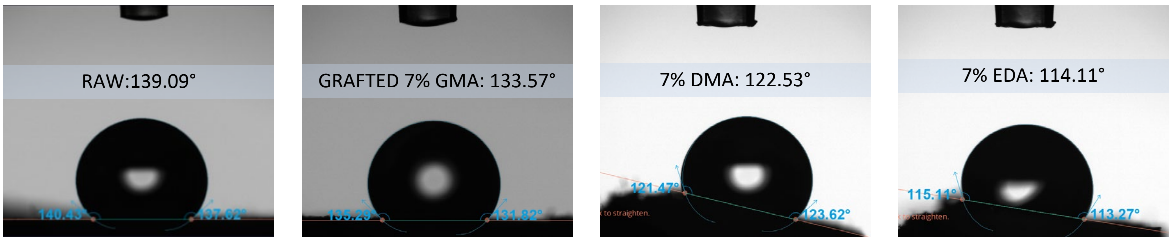


Figure 7(b). Contact angle for raw, grafted and modified industrial PE filter cartridge with 7 wt% of GMA

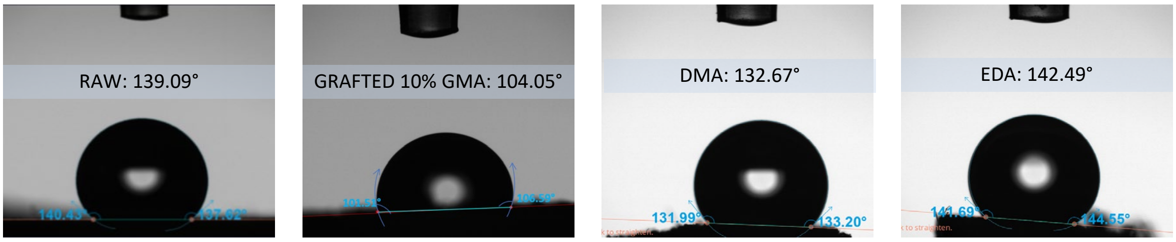
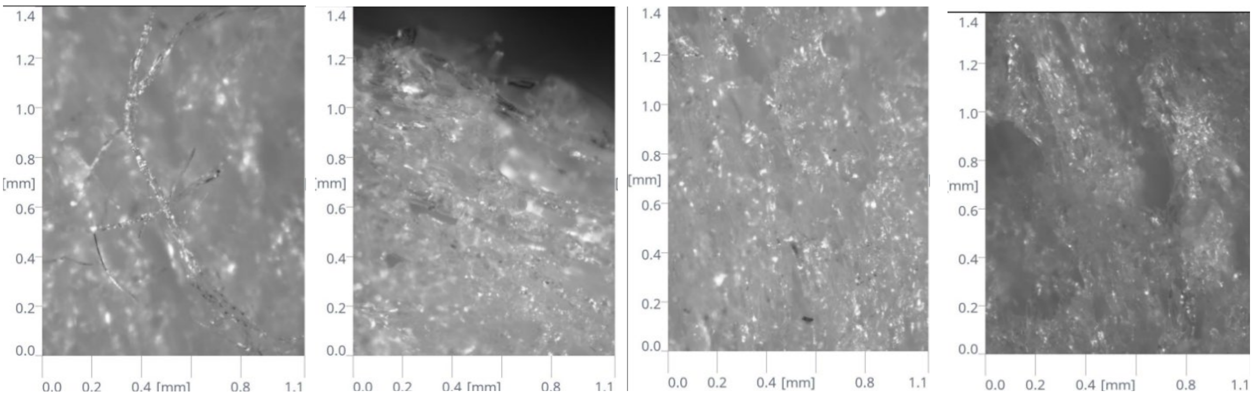


Figure 7(c). Contact angle for raw, grafted and modified industrial PE filter cartridge with 10 wt% of GMA

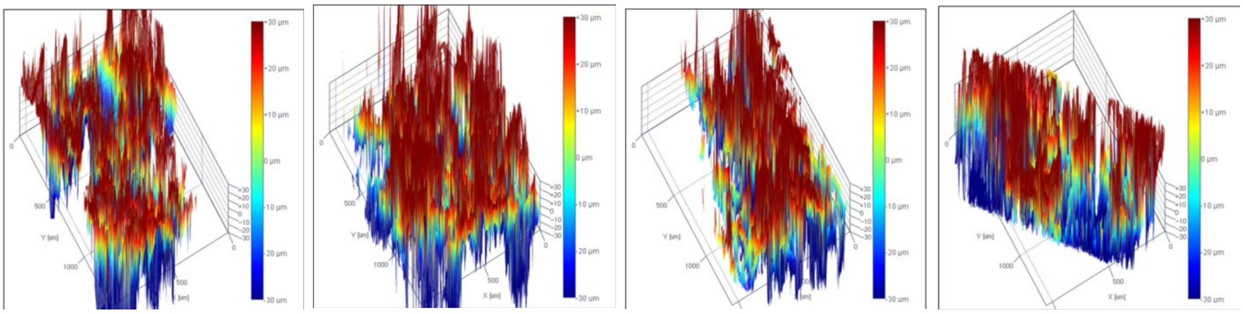
Surface Roughness on Water Contact Angle of Modified Industrial PE Filter Cartridge

Figure 8 and Fig.9 present optical images and 3D topography of the fractured surface for each sample, respectively.



(a) (b) (c) (d)

Figure 8. Optical images of the industrial PE filter cartridge samples: (a) raw, (b) g-7% GMA, (c) functionalized with DMA, g-7% GMA-DMA and (d) functionalized with EDA, g-7% GMA-EDA



(a) (b) (c) (d)

Figure 9. 3D reconstructed topography images of the industrial PE filter cartridge samples: (a) raw, (b) g-7% GMA, (c) functionalized with DMA, g-7% GMA-DMA and (d) functionalized with EDA, g-7% GMA-EDA

The root mean square roughness of surface topography (Sq) between the samples is 41.27 micron (µm) for raw, 41.48 µm for grafted with 7% GMA, 40.60 µm for functionalized g-7% GMA-DMA, and 44.05 m for functionalized g-7% GMA-EDA. Different types of materials have varying roughness levels based on their origin (Li et al, 2021; Stout et al., 2006). Therefore, raw, grafted, and functionalized industrial PE filter cartridges have naturally fractured surfaces with different roughnesses.

Table 1. Representative advanced contact angles with topography (Corrected Contact Angle, CAc) of 7% GMA concentration

Material (Industrial PE Filter cartridge)	Grafting Yield (%)	Contact Angle, CA (°)	Corrected Contact Angle, CAc (°)
Raw	-	139.09	93.75
g- 7% GMA	16.76	133.57	92.76
g-7% GMA- DMA	16.76	122.53	92.51
g-7% GMA- EDA	16.76	114.11	91.96

The contact angle (CA) and corrected contact angle (CAc) obtained for modified PE filter cartridges are shown in Table 1. Both CA and CAc showed a descending trend after grafting at 7% GMA and functionalization with DMA and EDA, respectively. The presence of carbonyl and amine groups during the modification process only reduces the contact angle. Ideally, the angle measured below 90° is perceived to be hydrophilic, and an angle above 90° is classified as hydrophobic (Li et al., 2021; Good, 1992). However, the CA values indicate that the sample surface is hydrophobic, even though it is decreasing. This is because the CA values are calculated based on Young's theory, which assumes the sample surface is ideal (absolute smoothness).

The CAc analysis is designed to measure the contact angle in consideration of the original surface roughness. Surface roughness topography values lead to CAc becoming more hydrophilic. As defined by Wenzel in 1936, the actual contact angle is determined based on the relationship between surface roughness and wettability. The increase in surface roughness will enhance wettability due to hydrophilic substances' surface composition (Erbil et al., 2014; Huang et al., 2010; Stout et al., 2006; Wenzel, 1936). Thus, the actual contact angle values of raw and modified industrial PE filter cartridges are measured by considering the roughness ratio.

CONCLUSION

The results indicate that the modification of an industrial PE filter cartridge as an adsorbent by simultaneous radiation-induced grafting using gamma radiation was successfully prepared and led to a decrease in hydrophobicity. Herein, a significant correlation between contact angle measurement and the attachment of functional groups (C=O and NH_2) to the surface material is established. This study indicates an increase in the wettability properties of the industrial PE filter cartridge as an adsorbent experimentally. Additionally, this study revealed the actual contact angle measurement of the material affected by surface roughness based on real surfaces using an advanced mode contact angle method. As a result of this discovery, the adsorbent's performance and functionality may be improved if it is combined with the desired wetting nature gained through simultaneous radiation-induced grafting.

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