Glow-discharge plasma enhanced coating and functionalization of needle-punched nonwoven PET filter media for textile wastewater decolorization

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Abstract. This study reports the use of glow-discharge plasma coated and functionalized PET needle-punched nonwovens as filter media for decolorization of textile dye-containing effluent. The investigation had been aimed at proving the possibility of GDP enhanced coating and functionalization (GDP processing) to produce better results for successfully replace such thermochemical finishing of PEI coat onto the primary PET fibers. The fiber surfaces functionalization with branched polymers such PEI has aroused much interest recently due to their unique properties as dye-immobilization absorber. For this study, the effect of processing time on the dye retention capacity of the functionalized PET nonwovens was investigated. Comparison was made between the most influential parameters of the basic, chemically and GDP processed PET nonwovens, such as: material thickness, air permeability, and puncture strength. The dye-retention capacity of the basic and functionalized nonwovens was determined by two synthetic water effluent – the anionic Orange G and the cationic Methylene Blue test-dyes have been used. The normal glow-discharge plasma processing in air as residual gas at 80 Pa provide the best possible anionic dye retention capacity. Based on this study, it was confirmed that this PEI coated and functionalized PET nonwoven could be used for the immobilization of anionic dyes from colored textile wastewater: the retention capacity from 4.16 to 5.57 mg/g with is comparable to the other available products used as adsorbent in dye-immobilization wastewater treatment.

1. Introduction
A large amount of water, chemicals, and dyes are used at textile wet processes, such as preparation, dyeing, finishing and laundry, with a high load of effluents, causing a high risk of water pollution. Dye removal has recently become of major scientific interest, as indicated by the multitude of related research reports. The increasing occurrence of many synthetic dyes in natural water led to the importance of using adsorption technique as one of the most effective methods of removing dyes from wastewater. Nonwoven filter media designing and developing are capable to improve the adsorption process with very high degree of filtration efficiency [1].

1.1. Nonwoven and functionalized nonwoven filter media
Functionalized nonwoven based filter media were designed to solve this problem. The usage of nonwoven filter fabrics varies according to their end use: they can be manufactured, with different parameters, concerning the nature of material, fiber denier, weight, and needle-punching manufacturing adjustment. The PET fibers have a very low surface free energy and for that reason they have non-polar
surface. Their application as dye filter materials was limited due to their lack of a chemical functional group which are averse to applications, such as liquid filtration and dye immobilization. Polyethyleneimine (PEI) is one of the most prominent examples of cationic polymers. Polyethyleneimine coated nonwoven fibers are important for achieving selective adsorption and immobilization of anionic dyes. It’s well known that epichlorohydrin (ECH) is a versatile precursor in a thermal finishing synthesis of branched PEI (bPEI) fiber coatings. Radical graft-polymerization of PEI impregnated over porous materials is an effective method for surface modification of inert and hydrophobic nonwovens [2, 3]. The functional PET fiber surfaces and polymers with branched structures such PEI have aroused much interest recently due to their unique properties and prominent applications in various fields of dye filtration and immobilization [4].

1.2. Glow-discharge plasma enhanced coating and functionalization

A. PEI could be effectively bound on the PET-fiber surface after a treatment in cold (non-equilibrium, non-thermal) glow discharge plasma [4]. Plasma-chemical activation introduces new functional groups to the surface. Free radicals are generated in these cold plasma surface treatments inducing a secondary reaction like cross-linking. Depending on the type of chemical groups plasma-chemical activation was used to obtain the desired new properties. A PEI branched monomer which is normally a liquid precursor undergoes a plasma polymerization on the surface. So, PEI could be effectively immobilized on various polymers pretreated by oxygen or air plasma [5]. By generating additional function after both PEI thermochemical and GDP coating and functionalization new material properties can achieve. The combination of both PEI polymer impregnation and GDP graft-polymerization lead to new surface properties of the fibers. In this way GDP processing leads to the plasma-chemical deposition of PEI coating with desired functional group on fiber surfaces. The used monomers (PEI and ECH) include functional groups and radicals such as hydroperoxyl anion radical (-COOH); amino group (-NH2), hydroxyl radical (-OH), epoxide group, etc. proper for dye wastewater immobilization.

B. GDP functionalization (activation) of PET nonwovens can be performed with various gases - argon, nitrogen, oxygen or residual air [2]. Based on the particle density, temperature, pressure, presence or absence of electromagnetic fields, different cold plasma state can be distinguished. The effect of GDP treatment on PET fibres leads to chemical, structural, and physical changes in the surface layers. In this study, we found that bPEI could be effectively immobilized on some PET nonwoven fibers after glow-discharge (air, oxygen) plasma processing of impregnated with PEI/EPI needle-punched nonwovens – GDP enhanced coating and functionalization. At the same time, those of the PET fibers of the nonwoven fabric, which are not coated, undergo GDP functionalization (activation). Large complex of ions on the PET non-coated surface appears after an oxidative GDP functionalization (activation, radical and functional group formation) of PET phenyl rings and polyethylene chains of mainly functional group formation: carboxyl (-C(=O)-OH) and carbonyl (C=O) groups, phenolic and alcoholic hydroxyl groups, and hydroperoxyl group (C-OOH) [6]. The GDP processing covers simultaneously as processing: i) the GDP enhanced PEI/ECH coating; ii) both the new PEI/ECH coating and bare PET surface functionalization. In general, there is a GDP enhanced processing of PET needle-punched nonwoven filter media for anionic and cationic dye immobilization and textile wastewater decolorization. The effect of GDP processing on PET nonwoven filter media is schematically shown in Figure 1.

The main idea of this paper was based on the concept that the anion/cation active dye will be immobilized on a functionalized filtration medium after the textile effluent containing the residual amount of dye comes into contact with the functionalized part of the PET fiber surface: a) the epoxide anion/cation active coating on the PET coating surface; b) the GDP chemically activated bare PET surface. Due to the newly formed PEI active centers, amino groups (-NH2), in combination with GDP functionalization of bare PET and the occurrence hydroxyl groups (-OH), the retention of anionic and cationic dye residues can be expected. In addition, the regeneration of a nonwoven filter by changing the pH of the nonwoven filter medium can be expected, due to differences in filtration and dyeing conditions.
2. Materials and methods

2.1. Basic PET needle-punched nonwoven medium

The experimental researches were carried out using PET (polyester) needle-punched nonwovens (NonWoTex Ltd., Bulgaria) with surface density (mass per unit area) of 500 g/m²; made by PET filaments with linear density (mass per unit length) – 6.7 dtex, and fiber length 57 mm. The main parameters of the basic (untreated) PET nonwoven are shown in Table 1.

| Parameter | Value | Unit |
|-----------|-------|------|
| Specific surface mass, EN 965 | 500 ± 8 % | kg/m² |
| Minimum average thickness at 2 Pa, EN ISO 5084 | 4.0 ± 0.4 | mm |
| Bulk density, EN ISO 9073-2 | 125 | kg/m³ |
| Tensile strength, EN ISO 13 934-1 | 18.1 | kN/m |
| Air permeability, EN ISO 9587 | 0.21 | m³/(m².s) |
| Punch density | 260 | needles/cm² |

2.2. Glow-discharge plasma coating and functionalization

The basic nonwoven sample (BS) was filled and cover (impregnated) on foulard at load of padder 43, 68, 91, and 113 kg with a mixture of PEI with molar mass 40.04 (repeat unit) and ECH with molar mass 92.52 g/mol. The basic samples were cut to a size of 200 x 200 ± 2 mm. After drying at 110°C for 90 min, the impregnated PET samples were treated in the cathode area of GDP at different pressure: 10, 20, 40, 80, and 100 Pa and time: 2.5; 5.0; 7.5 and 10 min. Different glow DC discharge modes – sub-normal (SGD) and normal (NGD) glow, were carried out by varying the residual gas (air) pressure, Figure 2. Comparison was made between the GDP-processed (PFS) and thermochemically processed (CFS) samples. The CFS samples went through the following operations: PEI/ECH mixture padding, drying (105°C), high-temperature condensation (160°C), and ultrasonic washing at about 40°C.

The PET nonwovens changes after GDP processing were determined by measuring the moisture absorption, mass and thickness changing, puncture resistance (EN ISO 12236:1999) and air permeability (Metrimex). Retention efficiency of basic, GDP- and thermochemically processed samples was determined by UV/VIS-spectrophotometry (Shimadzu) with two - cation and anion, synthetic test dyes: i) Methylene Blue: C₁₆H₁₈ClN₃S, MG 319.85, pH 8 and ii) Orange G: C₁₀H₁₀N₂Na₂O₇S₂, MG 452.38, pH 3. Methylene blue is a synthetic basic dye. Orange G also called Acid Orange G is a synthetic mono-azo dye.
3. Results and analysis

It was well known that PET fibers have very low surface free energy due to their non-polar surface. Therefore, PET fibers wet slightly, but this is not good for the water filtration. The PET fiber surface free energy was increased by two independent process: the first is the thermochemically bPEI processing and the second - the GDP-enhanced bPEI processing. Functionalized PET nonwovens become the ideal dye filter media. An bPEI nanolayer was formed on the PET surface, which alters the dye retention efficiency. In addition, improvement mechanical bonding and dimensional stability in use of the nonwovens were achieved. A very important feature is that the PET-fiber surface obtains an effective dye adsorption. The application of chemically bounded bPEI layer gives such an opportunity. 

Switching PET surface from hydrophobicity to hydrophilicity by GDP processing.

The moisture absorption capacity $B$ was determined to select the most effective GDP processing mode Figure 3.

| Glow discharge plasma pressure $p$, Pa | Sample mass $m_s$, g | $m_1$, g | $m_2$, g | $m_3$, g | $B$, % |
|--------------------------------------|----------------------|----------|----------|----------|-------|
| 10                                   | 5.33                 | 5.39     | 5.32     | 5.32     | 0.92  |
| 20                                   | 5.32                 | 5.36     | 5.32     | 5.32     | 0.85  |
| 40                                   | 5.01                 | 5.01     | 5.01     | 5.01     | 1.00  |
| 80                                   | 5.61                 | 5.61     | 5.61     | 5.61     | 1.32  |
| 100                                  | 5.33                 | 5.33     | 5.33     | 5.33     | 0.97  |

Figure 3. Nonwoven filter media with PEI coated and bare PET fiber surfaces switched by GDP processing from hydrophobicity to hydrophilicity are useful for die immobilization applications - the surface hydrophobicity reduction is illustrated very well by the observed increase of moisture absorption capacity $B$, %. Depending on the GDP pressure $p$, Pa, where: $m_s$ - mass of the basic sample; $m_1$ - mass of the PFS sample two hours after GDP processing; $m_2$ - mass of a PFS sample after one cycle humidification at 100 % humidity for 24 hours and drying; $m_3$ - mass of a PFS sample after two cycles of humidification and drying. NGD – normal GDP processing; SGD – subnormal GDP processing.

Samples with a diameter of 30 mm were processed. The GDP time was kept constant and equal to 25 minutes. Sample of basic PET material ($m_s$) was GDP processed ($m_1$) and then placed in a desiccator at 100 % humidity for 24 hours and after that was drying at 110°C ($m_2$) and again the humidification and drying procedure was repeated - sample ($m_3$). As the increased moisture absorption capacity $B$ is a
measure of the fiber surface hydrophobicity reduction after GDP processing and the ability to undergo chemical modification – the GDP processing mode at 80 Pa was selected for use. The moisture absorption capacity $B$ does not change significantly after moisturizing for 48 hours at 100% humidity, Figure 3. It can be seen also that after GDP processing, the mass of the treated nonwovens decreases as a result of fibers surface cleaning from different contamination and substances like finishing agents, lubricants, antistatic agents, etc. The moisture absorption capacity maximum coincides with the maximum of mass increase of PET sample at NGD pressure of 80 Pa, Figure 3.

3.1. **PEI/EPC liquid mixture padding process**

After partly filling the porous medium with PEI/EPC liquid mixture a squeeze processing mode was selected by determining the load on the upper foulard shaft of foulard machine. With less squeeze load, a part of the liquid mixture outflow. The amount of applied film depends on the degree of squeezing. PEI/EPC padding was formed on the fiber surface, Figure 4. The increase in mass $\Delta M$ of PET basic sample filling with the PEI/ECH liquid mixture before and after thermochemical processing are shown in Figure 4. Under these conditions, the thermochemical processing (condensation polymerization) was carried out at 160°C, after drying in advance at 105°C. This dried PEI/ECH padding was chemically active due to the presence of the amino groups (-NH$_2$) but after a thermal finishing in the presence of epichlorohydrin a solid insoluble PEI coating was formed. It changes PET surface morphology. The nonwoven becomes more rigid, stabilized in size and increased in puncture strength. These changes were determined by the amount of dry matter present in the porous volume. This amount depends on the degree of mechanically filled and equalized PEI/ECH liquid mixture over the whole height of nonwoven basic sample determined by the load on the upper shaft of squeezing padder (foulard machine). The maximum increase in mass $\Delta M$ of basic sample after thermochemical processing was implemented at the load of 8.85 kg on the upper shaft of squeezing padder, Figure 4.

![Figure 4. Increase in mass $\Delta M$ of nonwoven needle-punched PET basic sample (in blue) after thermochemical processing (in orange) with a liquid PEI/ECH liquid mixture and heat treatment during the following processing: drying at 105°C, condensation polymerisation at 160°C, and ultrasonic washing at about 40°C.](image)

3.2. **Glow discharge plasma processing of PET fiber surfaces**

Bi-component PET fibers were formed, with bare PET surface and PEI coated PET surfaces. The area ratio of these two PET surfaces depends on the squeeze load magnitude of foulard machine. The area ratio of these two fiber PET surfaces depends on the squeeze machine load. Both PET surfaces acquire different ionic activity due to their functionalization and the appearance of amino (-NH$_2$) and hydroxyl (-OH) groups. Some of the characteristics that can influence on the removal of textile dye waste are: adsorption capacity, specific surface area, and pore volume, expressed by air permeability. They are so important because if they change the effectiveness of removal also changes [7].

The thickness of GDP processed nonwovens increases and the material becomes larger as a result of the new active centers formation with the same electrical load and their mutual repulsion. After the filling and covering of the nonwoven porous media with PEI/ECH mixture under the squeezing load and the formation of a PEI coating the thickness of the PET nonwoven samples decreases Figure 5a. The changes of the nonwoven’s main characteristics after GDP processing (PFS) compared to the basic PET nonwoven (BS) and thermochemically processed nonwoven (CFS) characteristics are shown in...
Figure 5: the increase in the thickness (a), and puncture strength (b), and the slight increase in the air permeability compared to CFS (c), are well visible. The puncture strength increases compared to the thermochemically processed PET nonwoven in all the investigated cases, but decreases compared to the basic PET nonwoven with one exception at GDP pressure of 10 Pa - the highest puncture strength value was obtained, Figure 5a. This is probably due to the cross-linking process in the deposited layer, which is favoured by the applied GDP processing mode, in the area of the sub-normal glow discharge (SGD). After such SGD plasma functionalization at 10 Pa the basic (bare) PET nonwoven has the highest loss of mass. This means that the largest number of active centers were formed allowing the PEI/ECH layer to be crosslinked and a stable film was formed on the fiber surface. These circumstances leads also to the observed reduction in air permeability, Figure 5b. Probably the reason is the closure of some pores in the nonwoven volume.

The thickness of the coated and functionalized PET nonwoven decreases (blue columns), Figure 5c. The figure clearly illustrates the difference in PET nonwoven behaviour after GDP bare PET functionalisation and GDP coating and functionalization processing.

The results presented in Figure 6 refers to a single passage of two synthetic dye coloured (Orange G and Methylene Blue) effluents through a functional PET nonwoven filter. A comparative study was made between the retention anionic and cationic capacity of basic PET, thermochemically and GDP processing PET nonwovens. The basic and processed PET nonwovens are typical cation-functionalized filter media. The maximum anion dye retention capacity \( aRC \) sorts the three-filter media in the following order of increasing values \( aRC \): 1.29 (BS); 1.99 (CFS) and 5.86 (PFS) mg/g. The maximum cation dye retention capacity \( cRC \) ranges the three-filter media in the following order of increasing values of \( cRC \): 0.040 (BS); 0.044 (PFS) and 0.050 (CFS) mg/g, i.e. the maximum cation retention capacity of PET samples is incomparably smaller than their anion retention capacity: \( aRC >> cRC \) (\( aRC/cRC \) (80 Pa) = 5.76/0.035 = 164.6).
Figure 6. Relationship between the retention capacity RC of the basic PET nonwoven sample (BS), thermochemically (CFS) and GDP- (PFS) processed PET samples and the process factors: GDP-pressure p, Pa; and processing time t = 10 min = Const. The retention capacity was determined after the dye colored test water effluent passing through each sample once of two (anionic/cationic) test dyes – Orange G (orange columns), pH = 3, and Methylene blue (blue columns), pH= 8, onto the functionalized PET nonwoven surface.

The impact of processing time on the NGD plasma processing of PET nonwoven filter media from 2.5 to 10 min at constant in value NGD pressure (80 Pa) changes the results – the $aRC$ changes from 3.12 to 5.76 mg/g. From a technological point of view, the smaller the processing time is acceptable regardless of a not so bad result: 5.53 mg/g ($t = 5$ min) < 5.76 ($t = 10$ min): 5.53/5.76 x 100 = 96 %. At the same time, the processing time is twice less. These results require further investigation to ensure higher performance of the GDP enhanced coating and functionalization process.

The $aRC$ value of SGD plasma treated PET-nonwoven varies from 4.16 to 5.21 mg/g with pressure change from 10 to 40 Pa. The $aRC$ value of NGD plasma treated PET-nonwovens varies from 5.01 to 5.76 mg/g with pressure change from 80 to 100 Pa, Figure 6 a. These results for $aRC$ are closed to the well-known values of other filter media – 5.5÷5.7 mg/g, [4, 5, 8].

4. Conclusions

Glow discharge plasma enhanced processing (coating and functionalization) was used as a finishing for polyester (PET) nonwoven needle-punched filter media. The aim of this research was to find the possibilities of effective polyester non-woven coating and functionalization in order to manipulate the cation and anion immobilization activities relevant for textile wastewater treatment engineering. It is known that textile dye containing wastewater treatment is a process used to remove contaminants from wastewater and convert it into an effluent that can be returned to the water cycle with minimum impact on the environment:

(1) Glow discharge air (oxidative) plasma enhanced coating and functionalization is an universal tool for bPEI coating and functionalization of polyester filter media. It is a green or environmentally friendly technology for functionalization which refers the improvement in hydrophilicity, wettability, wicking, and ion immobilization activity for textile dye containing wastewater treatment.

(2) This study reports the use of GDP processed needle-punched PET nonwovens as filter media for decolorization of textile dye-containing wastewater. It proves the possibility of GDP enhanced coating to produce better results for successfully replace such thermochemical finishing of bPEI surface functionalized coating onto the primary PET fibers. Replacing the thermochemical process (at 160°C) energy consumption reduces. The low production costs, combined with higher dye retention capacity, make this GDP enhanced processing economical and effective. The PEI coated PET needle-punched nonwoven filter media with increased anionic dye (Orange G anionic synthetic water solution) retention capacity of 5.3÷5.76 mg/g is comparable to such filter available products.

(3) The GDP enhanced processing of PET nonwovens produces bifunctional PET fibers since the coating process allows partial surface coverage while leaving bare PET surface: i) branched PEI surface
functionalized (-NH₂) coating onto the primary PET fibers, and ii) plasma functionalized (-OH; -OOH) bare PET fiber surface. GDP enhanced bare PET functionalization is the first used surface functionalization effect at small processing times. After that the prolonged (5±10 minutes) GDP activation causes further etching resulting in the saturation of bare PET surface with functional groups. Polyester plasma functionalization does not produce one unique functionality - usually a distribution of different new functional groups and ion exchangers was produced – C-OH, C-O-OH, C=O, O=C- O-OH, C-O-, O=O-C–, C-H+, C-H₂O+, etc. The same glow discharge plasma functionalization procedure produces different concentration of functional groups and ions depending on the used glow regime – sub-normal (SGD) or normal glow (NGD) discharges plasma processing. Plasma activated bare parts of the fiber surface with its immediately increased functional groups and ion exchange capacity become also friendly to the soluble dye containing textile wastewater for physical immobilization on the nonwoven filter media.

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