

## IMMOBILIZATION OF HUMIC SUBSTANCES USING PLASMA MODIFICATION

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**ABSTRACT.** This paper presents a study of the immobilization of humic substances (HSs) on a polypropylene (PP) nonwoven fabric. In order to attach the HSs, the PP nonwoven fabric was modified in a volume of nonthermal atmospheric pressure dielectric barrier discharge (DBD) under defined conditions. An unmodified PP nonwoven fabric was used as a reference sample. The modified and unmodified samples were both dipped in an aqueous solution of potassium humate, and then the samples were washed in water and the amount of HSs attached to the PP fabric was monitored. An aqueous solution of cadmium salts was filtered through the treated fabric, the content of Cd<sup>2+</sup> in the solution was monitored using ICP-OES analysis, and the Cd<sup>2+</sup> sorbed on the fabric was proved by SEM/EDS analysis. The efficiency of the PP plasma modification was proved by XPS analysis, and the presence and the distribution of the HSs along the fibers was proved by SEM analysis.

**KEYWORDS:** DBD plasma modification; PP nonwoven fabric; humic substances; cadmium.

### 1. INTRODUCTION

In recent times, specialists have been taking increased interest in humic substances (HSs), because of their ability to absorb heavy metals, such as Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>.

HSs are the major *organic* constituents of soils, natural waters, river, lake and sea sediments, peat, brown-black coals and other natural materials as a product of chemical and biological transformations of animal and plant residues [1–7]. The interaction of humic substances with metals could play an important role in removing these hazardous substances from the environment [4, 6–10]. Many studies therefore focus on the interaction of heavy metals in wastewater with HSs [3–5, 8–12]. However, HSs are used mainly in powder form or in a solution, which limits their applications. It is therefore necessary to attach humic substances to porous carriers, which could be used as replaceable filters for filtering liquids or gases. HSs can be immobilized on a porous material by various methods, e.g., by chemical treatment or by plasma treatment. For plasma treatment, several plasma types can be used. The most widely used are low pressure plasmas [13] and atmospheric plasmas [14–16]. Low pressure plasma treatments usually allow better surface chemistry control, but quite complicated apparatus is needed. For our study, an atmospheric pressure dielectric barrier discharge (DBD) was used, because it can easily be brought into the production line, it has a relatively simple design, and there is no need for vacuum pumps, which are relatively expensive and also require long pumping times.

Our paper reports on the immobilization of humic substances (HSs) on a polypropylene (PP) nonwoven

fabric. In order to attach the HSs, the PP nonwoven fabric was modified in a volume of nonthermal atmospheric pressure DBD under defined conditions.

Cadmium, which is highly toxic to the environment, was selected for tests of the PP fabric with HSs for wastewater treatment. Cadmium in the form of salts contaminates wastewater and air. It is a major threat to human health, because it accumulates in tissues.

### 2. EXPERIMENTAL

#### 2.1. HUMIC SUBSTANCES (HSs)

Potassium humate was obtained from the raw material by alkaline extraction (KOH solution) at an elevated temperature, in the way described in detail in [3]. The raw material was young coal (oxyhumolite) from the Vaclav mine in North Bohemia (near Bilina).

The content of humic substances in a prepared sample was determined. The sample was subsequently diluted with water to a final content of 15% of HSs.

Analysis of the potassium humate: The chemical analyses followed standard chemical procedures, which are described in detail in [3]: water 79.62%; ash in dry state 29.88%; HSs in dry state 70.12%; pH 10, density 1111 kg/m<sup>3</sup>; HSs in dry state leachable: 69.82%; fulvic acids: 0.99%; total acidity of humic substances: 8.59 meq/g.

#### 2.2. POLYPROPYLENE (PP) NONWOVEN FABRIC

The PP nonwoven fabric was 0.5 mm in thickness and 0.019 g/cm<sup>2</sup> in density, and the diameter of a single fiber was 20 μm. For the experiments, a strip of nonwoven PP fabric 100 m in total length and 5 cm in width was used. The strip was cut into 4 parts used

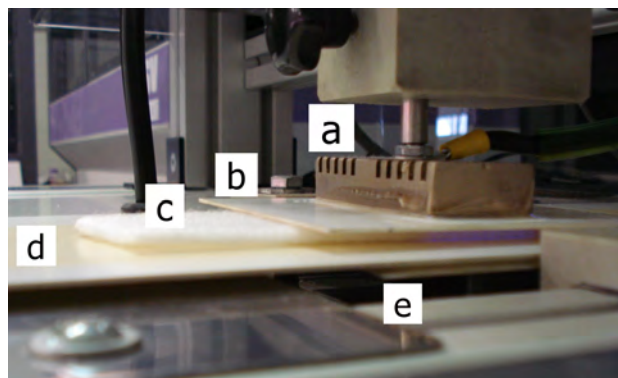


FIGURE 1. DBD Plasma reactor with parallel electrode alignment: a) powered electrode, b) dielectric barrier 1 – corundum, c) PP textile sample, d) dielectric barrier 2 – rubber, e) grounded electrode.

for 4 types of samples, as described in Section 2.5 – Method.

### 2.3. CHEMICALS

An aqueous solution of cadmium salts with a  $\text{Cd}^{2+}$  concentration of 1 mmol/l (112.4 mg/l) was used to determine the sorption capacity of plasma-modified and unmodified PP with and without humates.

A 7% acetic acid solution was used for acidification of the potassium humate.

### 2.4. PLASMA MODIFICATION

Dielectric barrier discharge treatments were conducted in air at atmospheric pressure, and the discharges were operated in filamentary mode, i.e., they were constituted by many tiny microdischarges (filaments) randomly distributed over the entire area of the electrodes. The plasma reactor (Fig. 1) consists of two plane parallel electrodes made from Ag80Cu alloy covered by a 1 mm layer of dielectric (corundum and rubber). Both electrodes are rectangular in shape, with dimensions of  $60 \times 50$  mm and thickness of 8 mm without active cooling. A detailed description is given, e.g., in [17]. The distance between the electrodes was 4.5 mm. The discharge was ignited by means of an AC power source, and filled the entire space between the electrodes. This means that the samples were completely immersed in the plasma.

Plasma treatment conditions and parameters:

- AC source voltage: 20 kV;
- AC source frequency: 3 kHz;
- nominal power: 120 W;
- distance of electrodes: 4.5 mm;
- modification time: 3 s;
- working gas: ambient air.

The efficiency of the plasma treatment of the PP fabrics was evaluated by the drop liquid test (Arcotest) and by an XPS analysis.

### 2.5. METHOD

The PP fabric samples were dried at  $105^\circ\text{C}$  for 1 hour to remove adsorbed water, and were then weighed and divided into 4 groups. The first group was modified in the DBD plasma for 3 s in order to increase the wettability and the adhesion of the HSs. Immediately after modification, the samples were immersed in the aqueous solution of potassium humate for 60 seconds, dried at room temperature for 24 hours and for 1 hour at  $105^\circ\text{C}$ . After weighing, the samples were dipped in acetic acid to stabilize the humic acids, and were then washed for 30 min in distilled water. Finally, the samples were dried and weighed again. This allowed us to determine the amount of immobilized humate on the PP fabric. The second group was prepared in the same way as the first group, but without plasma modification. The third and fourth group were the control samples, i.e., both were without humates - the third group was DBD plasma modified under the same conditions as the first group, and the fourth group was not plasma treated.

All 4 types of samples were tested for cadmium sorption capacity using the column apparatus. The column apparatus was filled with PP fabrics. Circular cuttings were used to fit the column. The total area of PP fabrics was  $62.8\text{ cm}^2$ , and it was dripped by an aqueous solution of cadmium salts with a flow rate of 0.5 ml/min. The resulting eluted solution was tested after each 1 ml for the presence of  $\text{Cd}^{2+}$ , using inductively coupled plasma optical emission spectrometry (ICP-OES). When the concentration of Cd at the column output reached the input concentration, the total amount of cadmium trapped in the column was used to determine the sorption capacity (i.e., the difference between the amount of Cd entering and exiting the column was measured).

The placement of the HSs on the fibers was observed by SEM analysis, and sorbed  $\text{Cd}^{2+}$  on the fabric was detected by SEM / EDS analysis.

### 3. RESULTS

The XPS analysis confirmed a significant change in the chemical composition of the surface of the PP fibers after DBD plasma modification. There were visible changes in the C1s peak (an increased signal corresponding to the carbon bonds with oxygen and OH groups). The deconvolutions were performed by comparing the spectra with the literature [18–20]. A quantification of the carbon and oxygen content using C1s and O1s signals is given in Tab. 1. Plasma modified PP fibers contained 14 at% of oxygen in comparison with 6 at% for unmodified PP fibers, and the O/C ratio of the modified fabric was more than 2.5 times higher. The literature [14–16] provides similar results for modified PP plasma at atmospheric pressure. The change in the chemical composition of the surface-modified PP fabric corresponds to its significantly increased wettability by an aqueous solution of potassium humate, and is consistent with the

PP fabric	Atomic concentration [%]		O/C ratio
	C1s	O1s	
PP unmodified	94	6	0.06
PP DBD modified 3s	86	14	0.16

TABLE 1. Atomic concentrations of carbon and oxygen for DBD modified and unmodified PP fabrics according to XPS. The C1s and O1s peaks were used for the quantifications.

PP/HS	Before washing	After washing				
	Content of HS [mg/cm <sup>2</sup> ]	Content of HS [mg/cm <sup>2</sup> ]	Content of HS/filling [mg]	Sorbed Cd [mg/filling]	Sorptive capacity [µgCd/cm <sup>2</sup> ]	Sorptive capacity [µgCd/mgHS]
Unmodified	32	3	188.4	0153	2.44	0.81
DBD modified	73	9	565.2	0.549	8.74	0.97

TABLE 2. Effectiveness of modifying fabrics with HSs.

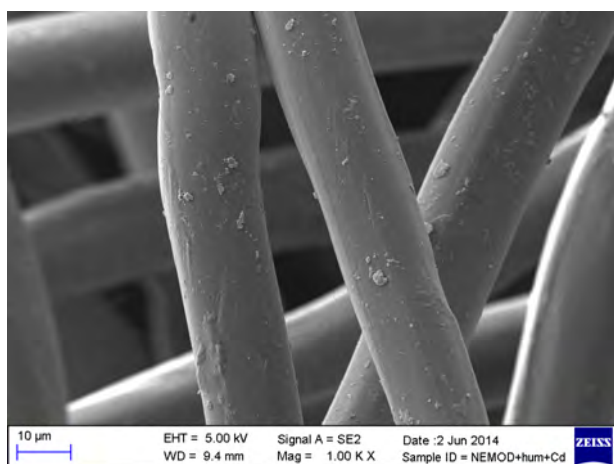


FIGURE 2. Placement of HSs on unmodified PP after washing.

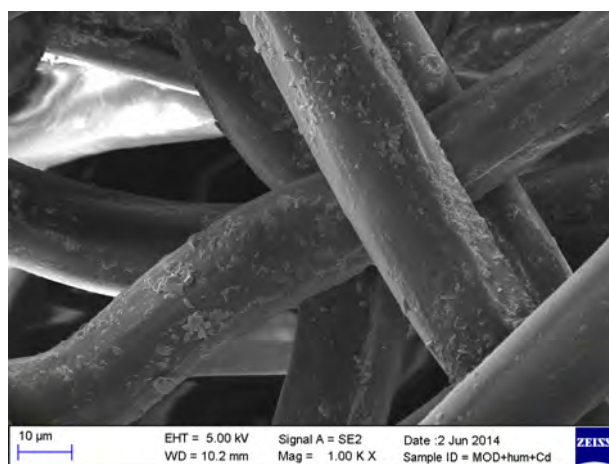


FIGURE 3. Placement of HSs on DBD-modified PP after washing.

increase in surface energy detected using the specified Arcotest liquids. The unmodified PP showed surface energy of only 28 mN/m, while the modified PP fabrics had surface energy more than twice higher (more than 56 mN/m) according to the Arcotest.

Due to the higher wettability of the modified PP fabrics, the modified samples retained a significantly higher amount of immobilized humate. Both groups of samples lost 90% of the humate after the PP fabrics were treated in acetic acid and washed in water. Plasma-treated PP retained 9 mg/cm<sup>2</sup> of HSs, in comparison with 3 mg/cm<sup>2</sup> of HSs immobilized on the unmodified fabric (Tab. 2). Figures 2 and 3 show an obvious difference in the distribution of immobilized particles of HSs on individual fabric fibers. There are particles of HSs very densely attached to the DBD-treated fabric, whereas the placement of the HSs on the fabric without treatment is sparse, confirming the effectiveness of DBD plasma treatment. There is a relatively good correlation between the triple amount

of HSs on the DBD-treated fabric and the 3.5 times higher amount (according to ICP-OES) of sorbed Cd<sup>2+</sup> in comparison with the unmodified fabric. The higher HS content allowed a greater amount of Cd to be captured, and in addition the distribution and the size of individual particles of HSs immobilized on the PP fabric can also have a positive influence on the Cd sorption capacity.

The amount of HSs was measured by weighing, and the amount of trapped cadmium was estimated by measuring the concentration of the Cd salt solution entering and exiting the column by ICP-OES (see Section 2.5).

Sorption of Cd<sup>2+</sup> on HSs particles was confirmed by an SEM/EDS analysis, see Figures 4 and 5, where Fig. 4 shows the same location as Fig. 3.

The experiments where the aqueous solution of cadmium salts was filtered through the PP fabric with immobilized HSs confirmed a positive effect of DBD modification of fabrics for increasing Cd<sup>2+</sup> filtration

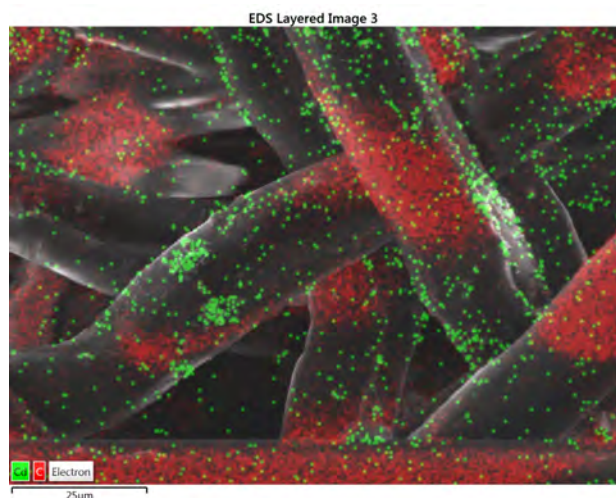


FIGURE 4. Placement of  $\text{Cd}^{2+}$  (green) on particles of HSs on DBD-modified PP after the experiment with an aqueous solution of Cd salts.

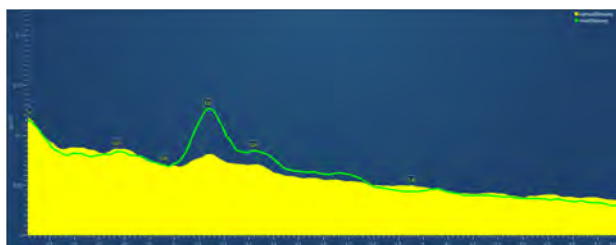


FIGURE 5. EDS of PP fabrics after adsorption of  $\text{Cd}^{2+}$ . Yellow indicates unmodified PP textiles with HSs, and green indicates DBD-modified PP textile with HSs.

efficiency. The cadmium concentration used in the solution was more than 100 times higher than the permissible limit for surface water. For a modified PP fabric with HSs, the eluted solution reached its original concentration after 25 ml had been dripped (Fig. 6), whereas for the unmodified fabric with HSs the eluted solution reached its original concentration after just 7 ml. In addition, for unmodified fabric with HSs, the HSs particles released together with sorbed  $\text{Cd}^{2+}$ , as indicated by following fluctuation of values in range 7–16 ml. In addition, for the unmodified fabric with HSs, the HSs particles were released together with sorbed  $\text{Cd}^{2+}$ , as indicated by the following subsequent fluctuation of values between 7–16 ml.

#### 4. CONCLUSION

Our experiments have confirmed the positive effect of DBD plasma treatment on immobilizing HSs on the PP non-woven fabric. DBD treatment of PP fabric increased the weight of the immobilized HSs on the fabric threefold in comparison with untreated PP fabrics. Modified fabrics with immobilized HSs show more than 3 times increased  $\text{Cd}^{2+}$  sorption capacity. These results can be very important in the field of wastewater treatment and air purification, and can

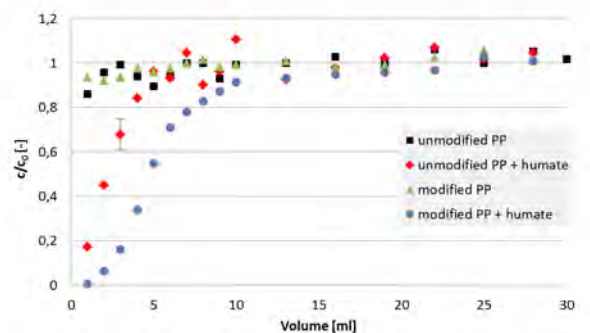


FIGURE 6. Dependence of the outlet  $\text{Cd}^{2+}$  concentration on the outlet volume of the working solution. For clarity, the error bar is given only for one data point. The other error bars are equal or smaller.

offer an economical and ecological solution for removing heavy metals, particularly cadmium, from the environment.

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