6. ULUSLARARASI MULTİDİSİPLİNER ÇALIŞMALARI KONGRESİ

6TH INTERNATIONAL MULTIDISCIPLINARY STUDIES CONGRESS

(26-27 Nisan 2019, Gaziantep, Türkiye)

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asos YAYINLARI

Surface Modified Polyacrylonitrile Nanofibers and Beads for Methylene Blue Removal

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Introduction

Many dyes and their degradation components are mutagenic, toxic, carcinogenic and teratogenic, creating in a huge threat to human health and aquatic life (Swaminathan, 2015). Thus, the removal of dyestuff from wastewaters has been carried out by several techniques such as membrane separation, coagulation, chemical oxidation, electricity, biological methods and adsorption (Rafatullah, 2010). Among the various techniques, adsorption is considered to be a cheaper, simple, attractive and favourable alternative method (Kahraman, 2017). This method can be used to remove different types of dyeing agents i.e., Methylene Blue (MB) from water sources.

The present study deals the compatibility of generated adsorbents in different forms for MB removal from wastewater. Polyacrylonitrile (PAN) was chosen to fabricate adsorbents in bead and nanofiber forms due to its binding ability, porosity, mechanical strength, etc. For this purpose, PAN nanofibers were prepared by electrospinning process and PAN beads were fabricated by phase inversion technique. After preparation of PAN based adsorbents in different forms, amine modification was performed to create an active surfaces and hydrophilic characters to the adsorbents. The physical and chemical properties of modified electrospun nanofiber and beads were characterized using FTIR and SEM analysis. Effect of various factors such as initial pH, concentration of adsorbents, dye concentration, and contact time, etc. on the adsorption of MB have been studied and discussed.

Experimental

Materials

Polyacrylonitrile (PAN) was chosen to fabricate adsorbents in the form of beads and nanofiber due to its binding ability, porosity, mechanical strength, etc. For this purpose, PAN nanofibers were prepared by electrospinning process and PAN beads were fabricated by phase inversion technique.

A cationic dye, methylene blue, having molecular formula $C_{16}H_{18}N_3SCl$ was chosen as an adsorbate due to its known strong adsorption onto solids. MB is the most commonly used dye for coloring cotton, wood and silk. MB also called tetramethylthionine chloride is a cationic dye and its degradation in natural environment is difficult.

Fabrication of Adsorbents

1.0 g of PAN was immersed into DMF (11 mL) solution to form a homogeneous gel after stirring at 60 °C for 2 h. Then it was allowed to mix for 16 h. Using a syringe, the PAN-DMF homogeneous gel turned into solid beads from the liquid phase in a glass culture dish with deionized water, the glass culture dish was shaken slightly to avoid the forming beads adhering with each other. Beads were washed with distilled water 3-4 times.

To prepare PAN nanofibers, PAN solution was prepared by dissolving 1 g of PAN into

11mL DMF. The solution was stirred on a magnetic stirrer at 60°C for 2h then it was allowed to stir for 16 hours. The prepared PAN solution was then added to a 5 mL plastic syringe and was electrospun using optimized electrospinning parameters.

To perform the modification of surfaces Ethylenediamine was used. EDA grafted PAN (E-PAN) was prepared by immersing PAN nanofibers and beads in EDA solution in 250-mL beaker and sealed. The mixture was heated and stirred on a water bath at 90-95°C. After the reaction, the mixture was cooled to 25°C.

Characterization of Adsorbents

SEM analysis was used to observe the surface morphologies of beads and nanofibers. As seen from the Figure 1, the surface of the bead is relatively smooth. The micrographs of E-PAN nanofibers exhibited similar surface morphology to that of the PAN mat without deterioration and degradation. It is attributed to the chemical grafting of EDA to PAN fibers.

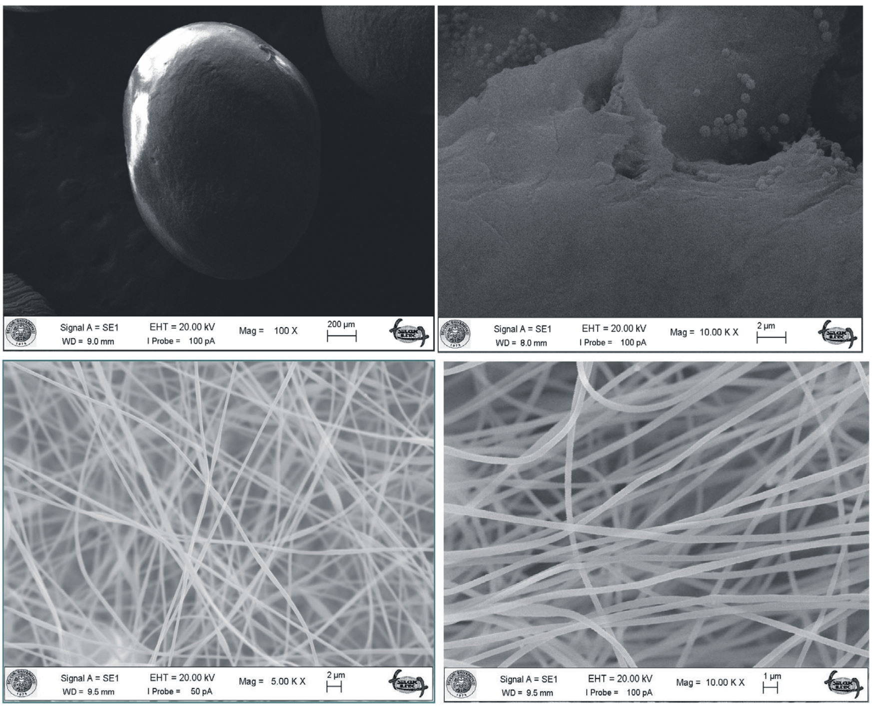

Figure 1. SEM micrograph of beads (a and b), PAN nanofibers (c), E-PAN nanofibers (d).

PAN exhibited the characteristic bands in region of 1000-1300 cm^{-1} (C-O stretching), at 1453 cm^{-1} (CH_2 bending), 1700 cm^{-1} (C=O stretching), 2241 cm^{-1} (C≡N stretching) and 2938 cm-1 (CH stretching). All the characteristic bands of PAN were observed in spectrum of EDA grafted PAN. The intensity of the sharp band at 2241 cm^{-1} continuously decreased until its intensity decreased, whereas the band at 1666 cm-1 is not only decreased but also shift to the lower frequency. A band at ~ 3300cm^{-1} attributed to the (N-H stretching). One new band at ~ 1480cm^{-1} (N-H bending) was also observed.

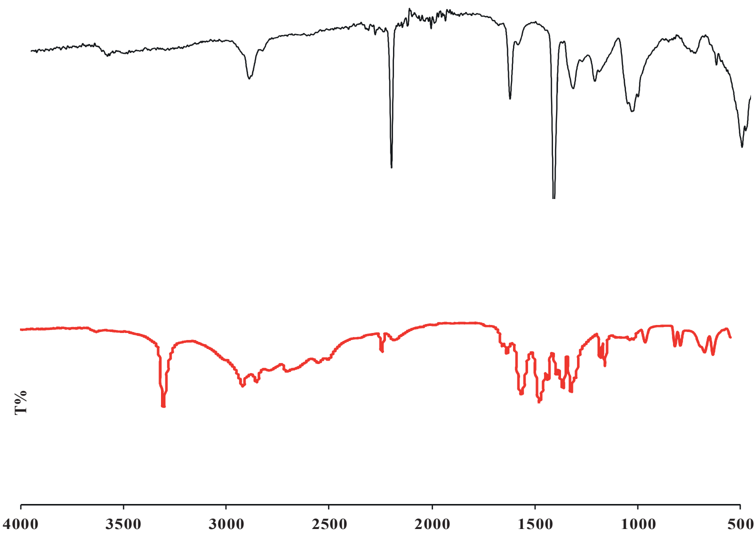

Figure 2. FT-IR analysis of PAN and E-PAN nanofibers.

Wettability is a significant property of any surface that identify the wetting ability, when the solid surface is exposed to liquid. Contact angle (C.A) is a quantitative measure of the wettability of a surface and it demonstrates significant change according to the surface energy and the solid surface roughness. For this purpose, in this study, the wettability of nanofibers was studied in water medium to figure out the behavior of the nanofiber when it is exposed to water. When water droplet was dropped on the surface of the nanofiber, it immediately spread on the surfaces (water contact angle, O.C.A, 0°).

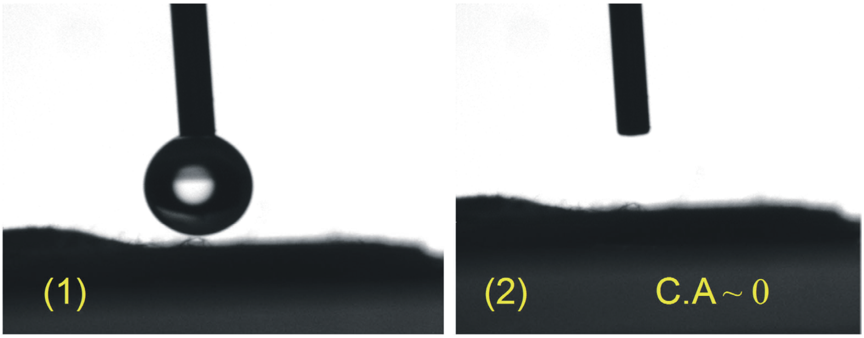

Figure 3. Water contact angle measurement of E-PAN nanofiber

Adsorption Studies

All chemicals were of an analytical grade. Double distilled water was used to prepare all solutions throughout the experiments. Solutions were stored in plastic sealed beakers. Solutions of 0.01 M NaOH and HCl (from Merck) were used for pH adjustment. Methylene blue concentration in the solution was analyzed with UV-vis Spectrophotometer (Scihmadzu UV-1700) (λ: 664 nm). Influences of parameters such as solution pH, adsorption time, concentration of adsorbent, and initial dye concentration on the removal of MB were studied.

Results and Discussion

Effect of pH

The maximum adsorption occurred at pH 8.0-10.0 for MB (Fig. 4). The maximum MB removal was 95% for nanofiber and 89% for bead at pH 8-10. The adsorption of MB on the surface of adsorbents depends strongly on the pH. As the pH increased from 2 to 8 the uptake of MB increased. This is an expected result because MB is a cationic dye. As the pH of the system increases and the number of negatively charged sites increase due to deprotonation of the surface. A negatively charged surface sites of adsorbents favors the adsorption of MB cations due to electrostatic attraction.

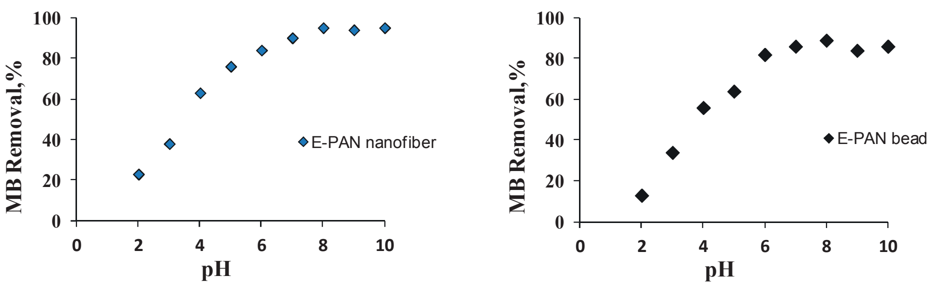

Figure 4. Effect of pH on removal of MB

Effect of contact time

Contact time is an important parameter to determine the time required to reach equilibrium during MB adsorption for efficient and economical water treatment processes. MB adsorption by PAN based materials was studied upon predetermined time interval. The adsorption of MB onto adsorbents presented in Fig. 5 as a function of contact time from 5 min to 300 min keeping other parameters such as temperature 25°C, pH 8; adsorbent doses 0.02 g and 0.04 g, for nanofiber and bead, respectively constant. The removal of MB increased with contact time until the equilibrium point for each adsorbent. Equilibrium is achieved in about 240 min for both adsorbents.

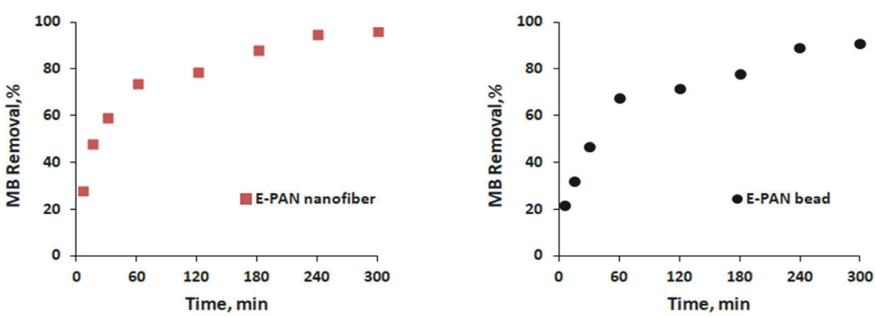

Figure 5. Effect of contact time on removal of MB

Effect of concentration of adsorbents

Concentration of adsorbent has great effect on the adsorption process as it determines the capacity of each adsorbent to remove a known initial concentration of dyestuff. The plot of adsorption capacities as a function of adsorbent concentration for nanofiber and bead are shown Fig. 6. Adsorption increased from 60 to 95% for nanofiber with increase in adsorbent dose from 0.1 to 1 g/L. The same trend was observed; 55 to 89% for bead with increase in adsorbent dose from 0.3 to 2 g/L.

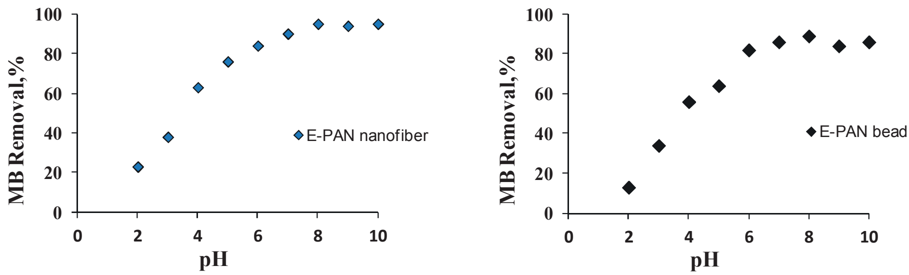

Figure 6. Effect of adsorbent dose on removal of MB

Effect of initial MB concentration

For this investigation, a series MB solution was used at various MB concentrations ranging from 20 to 200 mg/L. Effect of MB concentration on the removal by both adsorbents was investigated by varying the concentration (20-200 ppm) at a pH of 8 for 180-240 min equilibrium time. It can be seen an increase (Fig.7) in the initial MB concentration resulted in increased MB adsorption. Percent MB removal efficiencies of adsorbents increased with increasing MB concentration. At higher concentrations, MB molecules are left unadsorbed in solution due to the saturation of binding sites. Adsorption data of MB have been correlated with Langmuir and Freundlich models.

Langmuir and Freundlich isotherms have been both used to describe observed adsorption phenomena of MB on adsorbents. Adsorption capacities obtained with the application of Langmuir isotherm model were found as 63.24 mg g^{-1} for nanofiber and 58.8 mg g^{-1} for bead at pH of 8.

Due to the correlation coefficients were high for MB adsorption equilibrium state, can be seen in Table 1, the Langmuir-type isotherm was designated and MB uptake was calculated from the equation 0.198 mmol/g for E-PAN nanofiber and 0.184 mmol/g for E-PAN bead.

Table 1. Adsorption isotherm parameters

Adsorbent	*Freundlich Isotherm*			*Langmuir Isotherm*		
	K_f^a	n	R^2	K_b	A_s^a	R^2
E-PAN nanofiber	1.07	5.29	0.99	6321.3	0.198	0.99
E-PAN bead	0.79	3.71	0.98	4182.8	0.184	0.99

Conclusion

Nanofibrous PAN based adsorbent and PAN based microbeads were prepared using different methods. After preparation of PAN based adsorbents in different forms, amine modification was performed to create an active surfaces and hydrophilic characters to the adsorbents. Dye removal capabilities of produced adsorbents were investigated. This work showed that the adsorption of MB from aqueous solutions using E-PAN nanofiber and beads. The effect of various parameters, such as initial pH of dye solution, contact time and initial dye concentration was thoroughly investigated in simulated wastewater containing MB. Dye removal efficiencies of samples were 90-95% at the optimized pH 7-8. The adsorption process has been interpreted in terms of the Freundlich, and Langmuir isotherm models. Consequently, this work demonstrated that electrospun nanofibrous adsorbents and beads being highly efficient can be candidates for MB remediation in wastewater treatment.

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