SORPTION ISOTHERM STUDY ON TWO POLYAMIDE NANOFIBEROUS MEMBRANES

Yan WANG, Jakub WIENER, Guocheng ZHU

Technical University of Liberec, Faculty of Textile Engineering, Department of Textile Materials, Liberec, Czech Republic, yan.wang@tul.cz

Abstract

The aim of this study was to examine the different sorption properties between two polyamide 6 nanofibrous membranes. The electrospun polyamide 6 nanofibrous membranes with areal density respectively 1.26 and 2.90g/m^2 were used as the sorbent materials and the batch experiments were performed in room temperature for the sorption isotherm study. The acid dye (namely Color Index Acid blue 41) with concentration 0.01g/L was used. Experimental data was fitted with Langmuir and Freundlich isotherm respectively. BET test was taken for investigating the Nitrogen gas sorption property and the values of specific surface area. Result was compared and showed the BET surface area of sample A is 32.0m^2/g which is over 2.6 times larger than sample B. However, the batch experimental data showed similar sorption properties of both samples in dye sorption from aqueous solution. Freundlich isotherm showed steeper increasing trend than Langmuir isotherm. The correlation coefficient R^2 indicated that Langmuir isotherm fitted the experimental data better for both samples.

Keywords:

Isotherm; Polyamide nanofibers; Freundlich; Langmuir.

1. INTRODUCTION

Synthetic dyes have been extensively excreted in the wastewater from different industries, particularly from textile, paper, rubber, plastic, leather, cosmetic, food, and drug industries which used dyes to color their products.[1] Dyes are used everwhere in modern industrial society. The wastewater which contains big amount of soluble dyes caused plenty of environment problems [2]. Some biological and physical/chemical methods have been employed for dye wastewater treatment. Membrane filtration is one of the efficient treatments for adsorbing and seperating dyestuff from the textile effluents. Meanwhile the specific surface area is one of the most considered factors for adsorption properties of filter.

In this work, by examining the specific surface area from BET gas adsorption theory and sorption isotherms fitting after batch experiments, the correlation of sorption properties from aqueous solution with specific surface area would be discovered and discussed. Mophology of polyamide 6 nanofbrous membranes were examed by SEM images and the fiber diameters were mesured each 50 times and compared with specific surface area results. Constants and coefficient of determinations of fitted Freundlich and Langmuir isotherms were compared for both samples. And sorption propeties btween these two samples were discussed as well.

2. EXPERIMENT AND METHODS

2.1 Materials

2.1.1 Sorbent

Two kinds of electrospun polyamide 6 nanofibrous membranes(P6NM) purchased from ELMARCO s. r. o were used. The areal density were respectively 1.26 and 2.90g/m^2, and fiber diameter were 113±16, 187± 25nm. The morphology of the electrospun polyamide 6 membranes were observed by Scanning Electron Microscopy (SEM) and the fibres on the membranes were randomly selected to measure the individual fibre diameters by identifying two points at opposite ends of a fibre diameter for each sample 50 times.

2.1.2 Sorbate

Acid dye namely Acid blue 41 (AB41) was used in this work whose structure was shown below. The molecular weight is 487 g/mol and the molecular formula is $C_{23}H_{18}N_3NaO_6S$.[3] As a kind of water-soluble anionic dye, AB41 has good affinity for polyamide fibers.

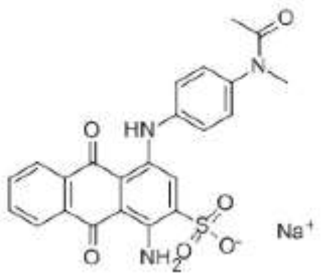


Figure 1: The molecular structures of C.I Acid blue 41.[4]

2.2 Testing methods

2.2.1 BET test

BET test was taken by Accelerated Surface Area and Porosimetry System, ASAP 2020, U.S.A. Nitrogen gas was used as the sorbate to measure the adsorption property of samples.

2.2.2 Batch test

Isotherm experiments were conducted in distilled water at pH 5.9±0.1. P6NM doses ranged from 20mg/L to 1000mg/L, and the initial AB41 concentration was 10mg/L, and the contact time was 10 days. The experiments were performed at a room temperature as 20±1ºC. At time t=0 and equilibrium, the dye concentrations of the solutions were measured by Spectrometer, spekol 11, zp100027. These data were used to calculate the adsorption capacity, C_S, of the adsorbent. Finally, C_S was plotted against equilibrium concentration, C_L.

2.3 Theory

2.3.1 BET

Based on Langmuir's one layer molecules adsorption equation, Brunauer, Emmett, and Teller derived the BET equation (Eq.(1)) from multimolecular adsorption theory that provided for calculation the number of adsorbate molecules in a monolayer.

$$\frac{1}{v\left[\left(p_0/p\right)-1\right]}=\frac{c-1}{v_m c}\left(\frac{p}{p_0}\right)+\frac{1}{v_m c} \qquad (1)$$

where v is the gas volume adsorbed at pressure p, v_m is the volume of gas required for a single molecular layer over the entire adsorbent surface, p_0 is the gas pressure required for saturation at the temperature of the experiment. c is the BET constant,

$$c=\exp\left(\frac{E_1-E_L}{RT}\right) \qquad (2)$$

where E_1 is the heat of adsorption for the first layer, and E_L is that for the second and higher layers and is equal to the heat of liquefaction. Specific surface area and the properties of the pores were calculated according to [5, 6].

2.3.2 Freundlich isotherm

The concave isotherm (‘‘L’’ or ‘‘H’’ isotherms) is the most widely met isotherm. The first model is empirical (Van Bemmelen, 1888; Freundlich, 1909)[7] and is based on the following relation between the adsorbed quantity C_S and the remained solute concentration C_L :

$$C_S = K_f C_L^{1/n} \qquad (3)$$

with K_f ((mg/g)(L/g)^n) and 1/*n* (heterogeneity factor, dimensionless) being two constants. The constant *n* may be either greater or less than unity, leading to isotherms which are either concave or convex to the bulk concentration axis.[8] This equation is easily linearizable (Eq. (4))[9, 10]

$$\log C_S = \log K_f + 1/n(\log C_L) \qquad (4)$$

The Freundlich equation predicts that the dye concentrations on the adsorbent will increase so long as there is an increased in the dye concentration in the liquid. [11]

2.3.3 Langmuir isotherm

Another very common model is based on reaction hypotheses (Langmuir, 1918). [7, 12] The Langmuir isotherm equation is:

$$C_S = \frac{q_0 K_L C_L}{1 + K_L C_L} \qquad (5)$$

where C_s is the sorption capacity of mass of dye per mass of fiber (mg/g), K_L is the affinity between sorbate and sorbent (L/g), C_L is the concentration in liquor (g/L), q_0 is the maximum amount of dye that can be adsorbed (mg/g). It can be linearlized by Eq. (6)[9]

$$C_S / C_L = 1/K_L q_0 + C_L / q_0 \qquad (6)$$

The Freundlich isotherm types are most often observed for adsorption from solution onto solids while the Langmuir isotherm is common to both liquid-solid and liquid-gas systems.[8]

3 RESULTS AND DISCUSSION

3.1 BET test

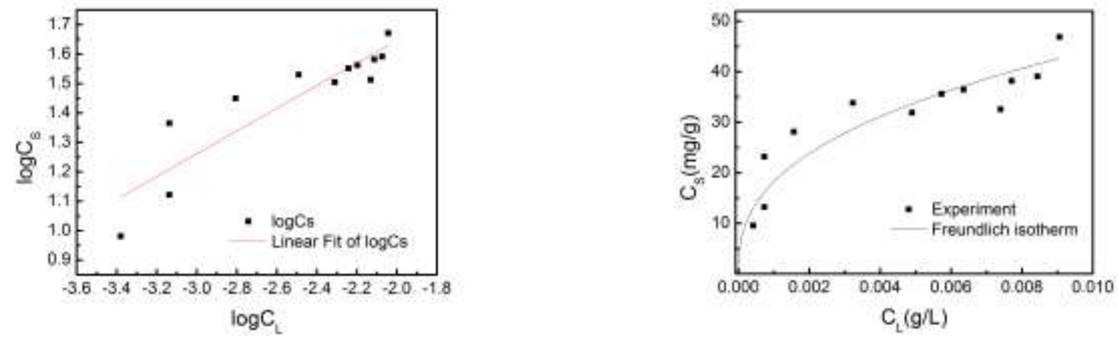
Table 1 shows the BET surface area of sample A is 32.0m^2/g, which is over 2.6 times larger than the BET surface area of sample B. It indicates a much better gas sorption properties of sample A.

Table 1: Testing results from BET test on two nanofibrous membranes.

Sample no.	Weight per Unit Area g/m^2	Diameter of nanofibers nm	BET Surface Area m^2/g
A	1.26	113±16	31.9980
B	2.90	187±25	12.1273

3.2 Sorption isotherms

The linear fitting of Freundlich isotherm for sample A was shown in Fig. 2 (a) with a relatively low squared corrilation coeffication 0.81.



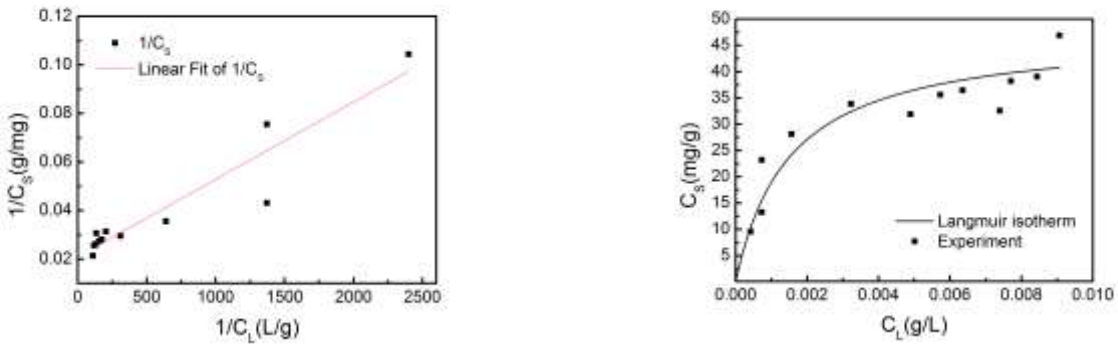
a b

Figure 2: Freundlich isotherm model applied on batch experiment results of sample A: a) Freundlich isotherm linear fitting; b) The experimental data compared with Freundlich isotherm model.

By linear fitting, the constants K_f and $1/n$ can be found through the slope and intercept values, with which the Eq. (4) coulbe be changed into Eq. (7) below:

$$C_S = 260.86 C_L^{0.39} \quad (7)$$

Figure 2 (b) showed the Freundlich isotherm drawn according to Eq. (7) comparing with the original experimental data.



a b

Figure 3: Langmuir isotherm model applied on batch experiment results of sample A: a) Langmuir isotherm linear fitting; b) The experimental data compared with Langmuir isotherm model.

Instead of Freundlich, the Langmuir isotherm linear fitting for sample A was applied and showed in Fig. 3 (a) with a squared corrilation coefficient compratively high and Eq. (8) could be found according to the constants calculated from the slope and intercept of linear fitting. Fig. 3 (b) showed the Langmuir isotherm compared with experimental data.

$$C_S = \frac{31451.29 C_L}{1 + 661.37 C_L} \quad (8)$$

Table 2 showed the constants and corrilation coefficients according to the results from both Freundlich and Langmuir isotherms fitting the experimental data for both samples.

Table 2: Equilibrium isotherm constants at room temperature.

Sample no.	K_f (mg/g)(L/g)^n	*1/n*	R^2 (Freundlich)	K_L L/mg	q_0 mg/g	R^2 (Langmuir)
A	260.86	0.39	0.81	661.37	47.55	0.88
B	270.96	0.34	0.84	1415.14	54.64	0.86

The constant q_0 stands for the maximum amount of dye that can be adsorbed in mg/g, which showed the sample B adsorbed more than sample A did which ion exchanging and chemical reaction can be involved to explain. In both samples case, constant n>1, the shape of the Freundlich isotherm for solid surfaces may be interpreted in terms of the latter's energetic heterogeneity, i.e., the highly energetic sites are covered first, etc., as bulk concentration of solute is increased.

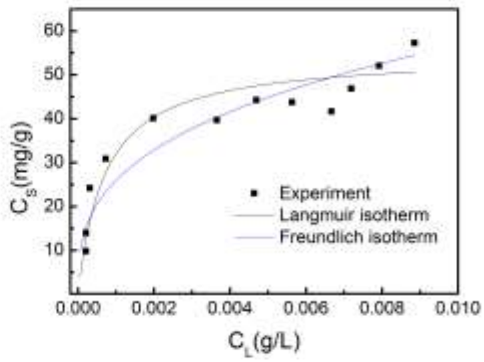


Figure 4: Comparision amoung Experimental data and two isotherm models.

Comparing the isotherms for sample B in Fig. 4, Freundlich isotherm showed steeper increasing trend than Langmuir isotherm. The coefficient of determination R^2 showed that Langmuir isotherm fitted the experimental data better. The Langmuir isotherm is often associated physically with adsorption onto an energetically uniform surface without lateral adsorbate interactions. The plateau is thought to correspond to a densely-packed adsorbate monolayer after whose formation there is no further adsorption. The mutual cooperation and cancellation of a variety of effects can lead to Langmuir-type adsorption. [8] However, in case of squared correlation coefficient lower than 0.9, a modified Langmuir isotherm or other more suitable isotherms may be studied and applied.

4 CONCLUSION

BET test showed the Nitrogen gas sorption properties on two polyamide 6 nanofibrous membranes which indicated the different specific surface areas. The values showed a negative correlation with fiber diameter of P6NM. However, according to the batch experimental data which was fitted with Freundlich and Langmuir isotherms, the dye sorption property from aqueous solution on both P6NM showed a negative correlation with specific surface area. Freundlich isotherm showed steeper increasing trend than Langmuir isotherm, meanwhile the squared correlation coefficient R^2 indicated that Langmuir isotherm fitted the experimental data better for both samples. However, more suitable isotherms are expected.

ACKNOWLEDGEMENTS

This study was financially supported under the SGS project with project no.: 21040 by Technical University of Liberec.

LITERATURE

[1] Ho, Y.S. and C.C. Chiang, Sorption studies of acid dye by mixed sorbents. *Adsorption-Journal of the International Adsorption Society*, 2001. 7(2): p. 139-147.

[2] Ferrero, F. and M. Periolatto, Functionalized fibrous materials for the removal of dyes. *Clean Technologies and Environmental Policy*, 2012. 14(3): p. 487-494.

[3] Wang, Y., J. Wiener, and G.C. Zhu, Langmuir Isotherm Models Applied to the Sorption of Acid Dyes from Effluent onto Polyamide Nanofibers. *Autex Research Journal*, 2013. 13(3): p. 95-98.

[4] Yan Wang, J.W., Guocheng Zhu. Adsorption property o f polyamide nanofibrous membrane on dyestuff for purifying wastewater. in NANOCON. 2013. Brno, Czech Republic: Tanger s.r.o.

[5] Barrett, E.P., L.G. Joyner, and P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances .1. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society*, 1951. 73(1): p. 373-380.

[6] Stephen Brunaauer, P.H.E., and Edward Teller, Adsorption of gases in multi-molecular layers. *Journal of the American Chemical Society*, 1938. 60: p. 309-319.

[7] Limousin, G., et al., Sorption isotherms: A review on physical bases, modeling and measurement. *Applied Geochemistry*, 2007. 22(2): p. 249-275.

[8] P. K. Chatterjee, B.S.G., *Textile Science and Technology 13, Absorbent Technology*. First ed. 2002: Elsevier Science B. V.

[9] Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*. 1984: John Wiley & Sons, Inc.

[10] HMF, F., Over the adsorption in solution. *Z Phys Chem*, 1906. 57: p. 385-471.

[11] Wong, Y.C., et al., Adsorption of acid dyes on chitosan - equilibrium isotherm analyses. *Process Biochemistry*, 2004. 39(6): p. 693-702.

[12] Langmuir, I., The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 1918. 40: p. 1361-403.