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Isotherm Studies for Performance Evaluation of Functionalized Carbon Nanotubes (CNT) Based Polymer Composite Nanofiltration Membranes for Desalination

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ABSTRACT

Composite Nanofiltration membranes were fabricated by incorporating Carbon Nanotubes (CNT) and Polyvinylidene Fluoride (PVDF) membranes. A suspension was prepared by dispersing CNT (30 minutes of sonication) in Dimethyl Sulfoxide (DMSO) solvent for 0.5 mg/ml. This suspension after vacuum filtration dispersed over PVDF membrane of pore size 0.22µm. Excess DMSO was removed by washing using Ethanol followed by Deionized water. Normal and various functionalized (Hydroxyl (-OH), Carboxylic (-COOH), Amine (-NH_2)) SWCNTs and MWCNTs were purchased and the CNT based polymer composite nanofiltration membranes were fabricated by vacuum filtration method at a uniform loading of 10mg/cm^2. The experimental results were used to evaluate the TDS removal efficiency of the fabricated membrane modules, which are normal and functionalized (4 composites in both SW and MW combinations) CNT. The TDS removal efficiency of all the 8 composite membranes were observed under varied operating conditions viz., varying flow rate (100,150,200 and 250 ml/hr) and influent TDS (2500, 3000, 4000 and 5000 mg/l). The flux of the membrane is varied 200 to 500 lit/m^2.hr. The Isotherm studies using the experimental data on Langmuir and Freundlich isotherm models validated the results of the experiment and are indicative of the role of adsorption of the functionalized CNT based polymer composite nanofiltration membranes which removing the TDS. The results showed that the amino functionalized SWCNTs based polymer composite (PVDF/SWCNTs) nanofiltration membranes can be used as an effective adsorbent for desalination due to their high adsorption capacity.

***Keywords* -** Adsorption capacity, Carbon Nanotubes, Desalination, Freundlich Isotherm, Langmuir Isotherm, Polyvinylidene fluoride.

I. INTRODUCTION

Membranes have been extensively used for the removal of various contaminants present in water. Successful attempts were done to incorporate different fillers like titania, silica, alumina, and CNT in polymeric membranes for improving the separation performance and resistance against fouling and compaction phenomena. In Earlier studies, CNT sheets were synthesized by chemical vapour deposition and oxidized with nitric acid at room temperature and then employed as a practical adsorbent for salt water desalination and it was found that the adsorption capacity of the CNT sheets increases significantly after oxidization process. Recently back washable CNT mats were generated on the inner surface of polymeric hollow fibre membranes and the fouling resistance and contaminant removal capabilities were investigated.

In the present work, synthesis and evaluation of functionalized CNT based polymer composite nanofiltration membranes were fabricated to study their performance for desalination using the dead - end filtration system, with various parameters like TDS removal, water flux and pressure. Effects of adsorption with varied feed salt concentration on the performance of the composite membranes were experimentally investigated. The results were used in Langmuir and Freundlich Isotherms to evaluate the adsorption characteristics of the different combinations of CNT based polymer composite nanofiltration membranes.

II. MATERIALS AND METHODS

2.1 Materials

SWCNTs and MWCNTs were purchased from Nanoshell LLC, Wilmington DE. The hydrophilic PVDF membrane (pore size 0.22 µm and having a thickness of 120 µm) was from Millipore. DMSO (HPLC grade), Ethanol and Sodium Chloride were from Sigma Aldrich.

2.2 Membrane Fabrication

Functionalized CNT based polymer composite nanofiltration membranes were synthesized by vacuum filtration method. Required amount of CNT were dispersed in DMSO solvent to a concentration of 0.5 mg/ml. After that the suspension was sonicated (30 minutes) in a water bath sonicator, the suspension was filtered through vacuum filtration. The well dispersed suspension was deposited on a PVDF membrane of 25mm diameter. Subsequently, Ethanol followed by De-ionized water was passed through the membrane for the excess removal of DMSO. CNT based polymer composite nanofiltration membranes using normal and various functionalized (-OH, -COOH, $-NH_2$) SWCNTs and MWCNTs were fabricated by vacuum filtration method for uniform CNT loading of $10mg/cm^2$.

2.3 Experimental Setup

The schematic of the experimental setup is presented in Fig.2.1. The experimental set up principally has the fabricated modular Nanofiltration filtration system with 25mm membrane filter holder assembly with the membrane effective surface area of 1.7 cm^2. The CNT based polymer composite nanofiltration membrane was mounted on the filter holder and the membrane was fixed in position with the use of clamp. The feed water was pumped through the membrane by means of a peristaltic pump for varied inflow rate of 100,150,200 and 250 lit/hr and the permeate water was collected. Pressure gauge was fitted in the pipe to measure the pressure variations.

2.4 Experimental Methodlogy

The experimental results were used to evaluate the TDS removal efficiency of the fabricated membrane modules, which are normal and functionalized (4 composites in both SW and MW combinations) of CNT. The TDS is imparted by dissolving sodium chloride at required levels. The TDS removal efficiency of all the 8 composite membranes were observed under varied operating conditions viz., varying flow rate (100,150,200 and 250 ml/hr) and influent TDS (2500, 3000, 4000 and 5000 mg/l). The flux of the membrane is varied 200 to 500 $lit/m^2.hr$. The Isotherm study was carried out using experimental data for all combinations of composite membranes and under all operating conditions of varied flow rate and influent TDS.

III. ADSORPTION ISOTHERMS

3.1 Langumir Adsorption Isotherms

The adsorption Isotherm of Langmuir is represented as

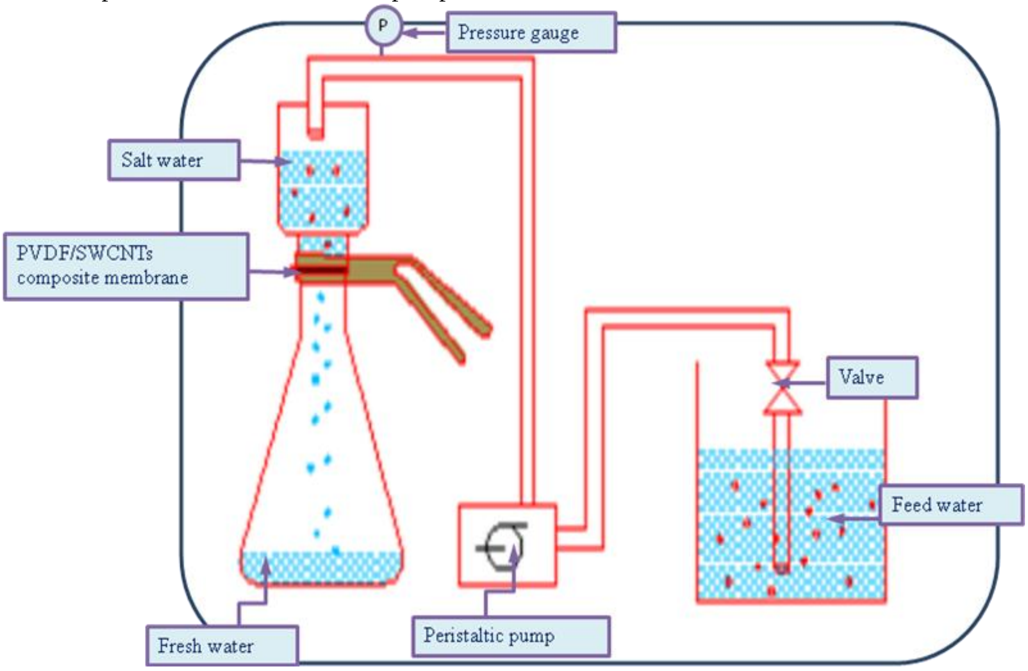

Figure 2.1 Schematic of the experiment setup

$$\frac{x}{m} = \frac{q_m b C_e}{1 + b C_e} \quad \text{..... .... (1)}$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation into linear form

$$\frac{1}{\frac{x}{m}} = \frac{1}{q_m} + \frac{1}{q_m b\ C_e} \quad \text{... ..... (2)}$$

Where: C_e = the equilibrium concentration of adsorbate (mg/L)

x/m = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).
q_m = maximum monolayer coverage capacity (mg/g)
b = Langmuir isotherm constant (L/mg).

The values of q_m and b were computed from the slope and intercept of the Langmuir plot of 1/(x/m) versus $1/c_e$. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred as separation factor or equilibrium parameter

$$R_L = \frac{1}{1+(1+bC_0)} \qquad \text{............... (3)}$$

Where: Co = initial concentration
b = the constant related to the energy of adsorption (Langmuir Constant).
R_L value indicates the adsorption nature to be either unfavourable if R_L>1),
linear if R_L =1,
favourable if 0< R_L<1 and
Irreversible if R_L=0.

3.2 Freundlich Adsorption Isotherms

Freundlich Isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich

$$q_m = K_f C_e^{1/n} \qquad \text{...……….. (4)}$$

Where K_f = Freundlich isotherm constant (mg/g)
n = adsorption intensity;

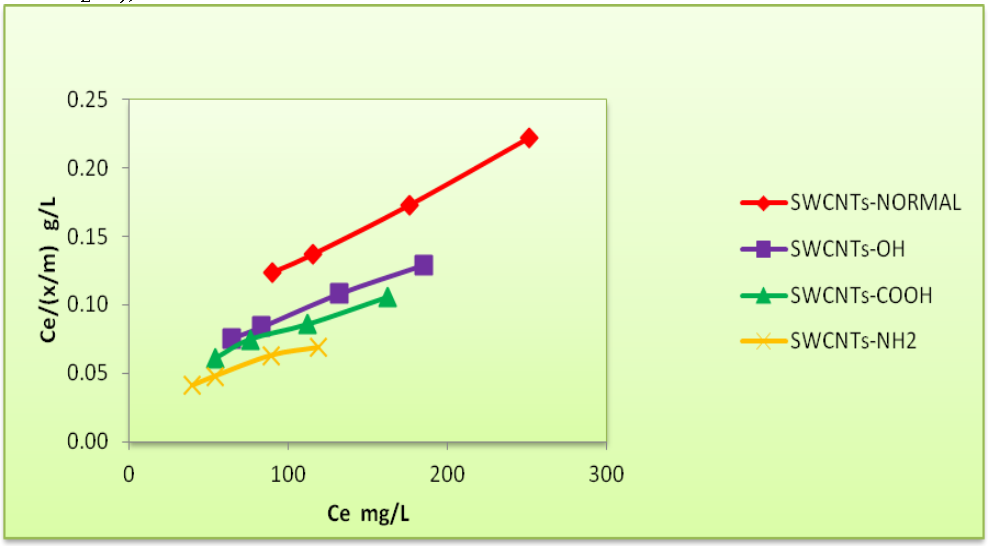

Figure 4.1 Langmuir isotherm curve for PVDF/SWCNTs nanofiltration membranes.

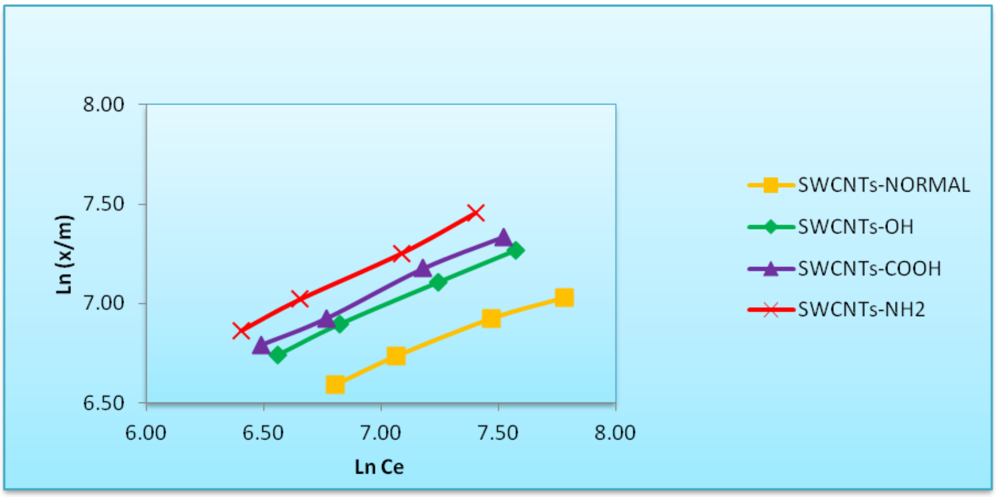

Figure 4.2. Freundlich isotherm curve for PVDF/SWCNTs nanofiltration membranes.

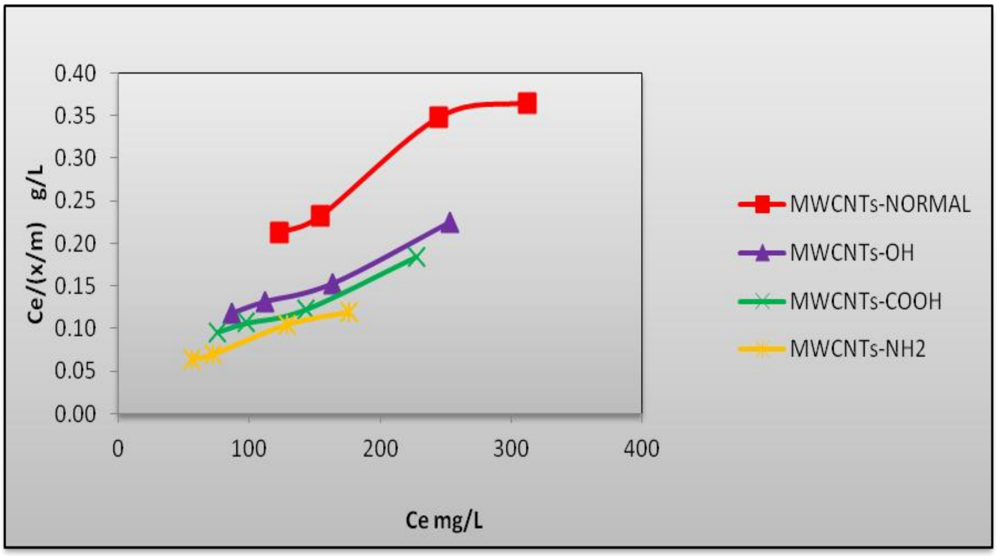

Figure 4.3 Langmuir isotherm curve for PVDF/MWCNTs nanofiltration membranes.

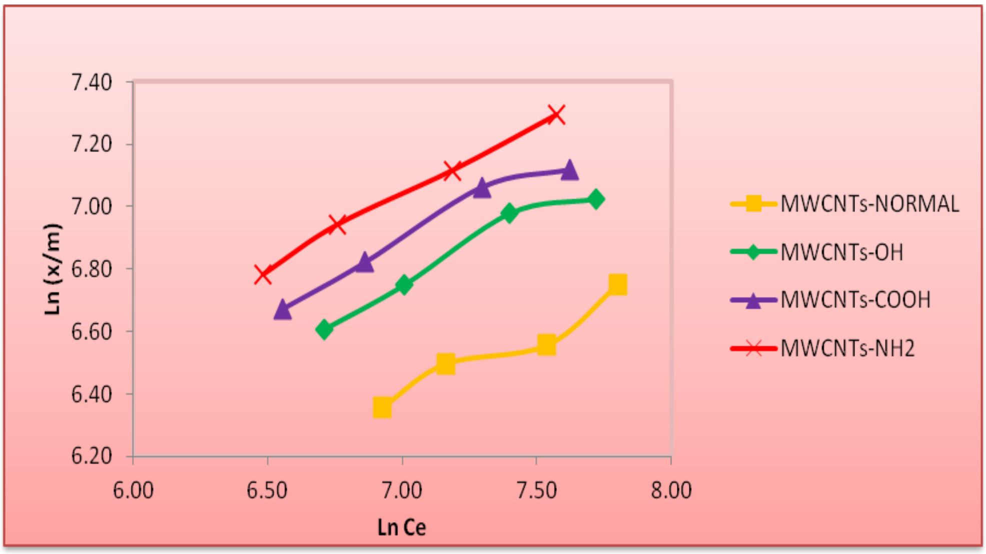

Figure 4.4 Freundlich isotherm curve for PVDF/MWCNTs nanofiltration membranes.

C_e = the equilibrium concentration of adsorbate (mg/L)

q_m = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

Linearizing equation, we have

$$\log q_m = \log K_f + \frac{1}{n} \log C_e \qquad \ldots\ldots (5)$$

The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption. If n lies between one and ten, this indicates a favorable adsorption process.

IV. RESULTS AND DISCUSSION

4.1 Adsorption capacity of SWCNTs based polymer composite (PVDF/SWCNTs) nanofiltration membranes.

Fig. 4.1 shows the Langmuir isotherm curve for PVDF/SWCNTs nanofiltration membranes. The maximum monolayer coverage capacity (q_m) from Langmuir Isotherm model was determined to be 2825 mg/g. The Langmuir isotherm constant (b) is 0.012 l/mg. The separation factor (R_L) is 0.243. Hence, the results are indicative for favorable equilibrium adsorption and the R^2 value is 0.951 which validates the adsorption data, fitting well with the Langmuir Isotherm.

Fig. 4.2 shows the freundlich isotherm curve for PVDF/SWCNTs nanofiltration membranes. From the Freundlich isotherm, the value of 1/n is 0.581

while n is 1.71. This is indicative of adsorption for salt removal and the R^2 value is 0.996.

4.2 Adsorption capacity of MWCNTs based polymer composite (PVDF/MWCNTs) nanofiltration membranes.

Fig. 4.3 shows the Langmuir isotherm curve for PVDF/MWCNTs nanofiltration membranes. The maximum monolayer coverage capacity (q_m) from Langmuir Isotherm model was determined to be 2045 mg/g. The Langmuir isotherm constant (b) is 0.0134 L/mg and the separation factor (R_L) is 0.223. These results are indicative for a favorable equilibrium adsorption and the R^2 value is 0.982, proving the adsorption data fitted well with Langmuir Isotherm model. Fig. 4.4 shows the Freundlich isotherm curve for PVDF/MWCNTs nanofiltration membranes. From the Freundlich isotherm, the value of 1/n is 0.459 while n is 2.17 indicating that the adsorption of salt is favored with R^2 value at 0.996.

V. CONCLUSION

The synthesis and TDS removal efficiency of functionalized CNT based polymer composite nanofiltration membranes were examined with an experimental set up to study its performance as TDS removal efficiency under varied operating conditions of influent TDS, different functionalization and range of flux. The Isotherm studies using the experimental data on Langmuir and Freundlich isotherm models validated the results of the experiment and are indicative of the role of adsorption of the membranes which removing the TDS.

The results showed that amino functionalized (PVDF/SWCNTs) nanofiltration membranes can be used as an effective adsorbent for desalination due to their high adsorption capacity.

The experimental results are proof for CNT based membranes are fit for water desalination. The results revealed that PVDF/SWCNTs composite membranes are a promising alternative to pressure and energy intensive- membrane technology. Nevertheless, further work is needed to evaluate the fouling characteristics and regeneration of the membranes.

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