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Research Article

SEPARATION OF NITROCELLULOSE USING INORGANIC MEMBRANE (MF/NF) SEPARATION SYSTEM

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ABSTRACT

Nitrocellulose (NC) is a basic constituent for military gun propellants and has civilian applications in photographic films and paints. NC wastewater is a by-product of the NC manufacturing process. The environmental impact of NC is currently a major concern, mainly due to its higher reactivity and toxicity, a fact that makes this compound highly harmful. A pilot-scale microfiltration and nanoflitration (MF/ NF) filtration system was constructed to study the feasibility of NC recovery from the industrial wastewater generated from NC manufacture process. Batch concentration mode experiments were performed on the synthetic and real wastewater at different operating parameters. The performance of the MF and NF membranes was evaluated in terms of TSS, TDS, TOC, COD and UV absorbance, conductivity and turbidity. The scanning electron microscope (SEM) for both the original and used membranes showed that the MF membrane was fouled only by NC fines the MF/NF process, allowed the recovery of NC fine from industrial wastewater and reuse more than 80% of the original wastewater. The quality of NF permeates obtained at trans membrane pressure of 5 bar and crossflow velocity 7 m/s showed low values of salts: 300 mg/L, conductivity: 290 µS/cm, COD less than 5 mg/L. and non-detected TOC. The permeate quality obtained from MF/NF system in the present work satisfied with the Egyptian Environmental Law (Law 4/1994). Empirical correlations have been developed to permit quantitative estimation of flux based on prevailing operating conditions. Further, quantitative analysis of fouling resistance has been developed with emphasis on the contribution of the different components of the resistance namely Rc, Rm, Ri and Rt. The results in general confirm that technical feasibility of concentration and recycling of NC fines and the recovery of high quality clean water based on MF, NF inorganic membranes.

INTRODUCTION

Separation of nitrocellulose fines (NC) from process wastewater streams can be applied as a treatment technology in itself, or as a pre-treatment step followed by chemical or physical alteration of the concentrated material. In cases where chemical or physical alteration of the nitrocellulose is proposed, concentration of these materials is a vital first step in making any such technology economical. Separation methods looked at in recent studies includes sliding bowl centrifugation, solid bowl centrifugation, pressure filtration, new decanters, and microfiltration (Kim and Park, 1993; Kim and Park, 1993).

In 1987, Arthur D. Little, Inc. was contracted by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) to perform engineering and cost evaluation for the separation and treatment of these nitrocellulose wastes at the Radford Army

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Ammunition Plant (RAAP) in Radford, VA. Arthur D. Little, Inc. (Balasco, 1987) evaluated the performance of both sliding bowl and solid bowl centrifuges at RAAP. Pilot scale evaluations using DeLaval sliding bowl centrifuges, installed for the purpose of clarifying the poacher pit water, showed promise. However, continuous operation of these centrifuges proved to be unreliable due to inconsistencies in particle removal efficiency, and the accumulation and sticking of solids to the bowls of the centrifuges. Solid bowl centrifuges were also evaluated as a means to further concentrate the waste stream that had been preconcentrated by the sliding bowl centrifuges. It was anticipated that such a secondary concentration step would yield sludge containing 20 to 25 percent NC solids. The solid bowl centrifuges operated in this manner also failed to perform adequately. This was due to the failure of the sliding bowl centrifuges to sufficiently preconcentrate the waste stream.

Polymers were used in the experiments to determine optimum type and dosage required for effective treatment of an industrial effluent containing nitrocellulose fine particles. It was found that contact flocculation filtration was not effective for treating the nitrocellulose manufacturing waste-water due to the high initial turbidity. Mixing, flocculation, and settling of the wastewater with cationic polyelectrolyte and bentonite clay gave greater than 95% turbidity removal. Optimum chemical dosages, mixing, flocculation, sedimentation and filtration removed 99.9% of the wastewater turbidity (Shuster, *et al*., 1982).

Crossflow microfiltration/ultrafiltration (MF/UF) may recover NC fines and allow the wastewater to be recycled. This bench-scale crossflow membrane filtration system was constructed to test the application of MF/UF technology to NC wastewater.

(Byung, *et al*., 1997) concluded that: UF membranes have a lower flux decline rate and a higher flux recovery than MF membranes but, UF membranes have a relatively low permeate production rate compared to MF membranes. Also, a critical membrane pore size of about 0.1 um exists, at which point the worst flux performance occurs.

Finally, the cellulose-based hydrophilic membranes have the best flux performance (Byung, *et al*., 1997).

EXPERIMENTAL INVESTIGATIONS

Materials

The tested fluids used with the investigated MF as follows:

1. Synthetic NC solution of two different types (A and B) samples prepared by dissolving NC powder with concentrations from 100 – 400 mg/L.

2. Two different types (A and B) of NC real wastewater samples which are generated from the centrifugation and washing stages and characterized with nitrogen content of 11.8% and 12.8%, respectively.

3. Membrane cleaning solutions (2% NaOH, 1% HNO_3, 0.7% ultrasil 11 and 0.5% ultrasil 75.

4. Tubular MF inorganic membrane manufactured by Rhodia Orelis, Miri, France. The physical and chemical specifications are depicted in Table 1.

The experimental procedure involves determination of the permeation rate and flux at different operating pressures (from 0.5–2 bar) Further, the effect of cross flow velocity and NC concentration was explored. The perrmeate from MF was collected to evaluate the MF permeate quality. After each run, the system is cleaned using the appropriate solution until restoring the initial water flux.

Experimental system

The pilot-scale system comprises two stainless-steel housings one for MF tubular membrane module and other module is standby, 50 L stainless-steel 316L feed tank, air compressor model HAC200/380 Haggar industrial Egypt, feed pump (diaphragm pump), Wilden company U.S.A, cartridge filter and multi stage centrifugal pump S.A.R.L, Germany. The system is equipped with digital flow meter, two pressure transducers (0–10 bar) located at the inlet and outlet of the membrane module, temperature sensor and control panel. The flow sheet of the pilot unit is shown in (Fig. 1)

ANALYSIS AND CHARACTERIZATION

Analysis

The NC simulated wastewater samples permeates and retentate of MF were analysed according to the following analytical methods:

Table 1. Physical and chemical specifications of MF membrane.

Property	MF
Membrane material	ZrO_2
Support	Carbon
Configuration: channel tubular	7 flows
Membrane surface area, (m2)	0.16
Molecular weight cut-off (MWCO)	0.14 µm
Operating pressure TMP, (bar)	up to 15
Max. operating temperature	up to 100°C
pH operating range	0-14
Dimension	10mm(D)×1200 mm

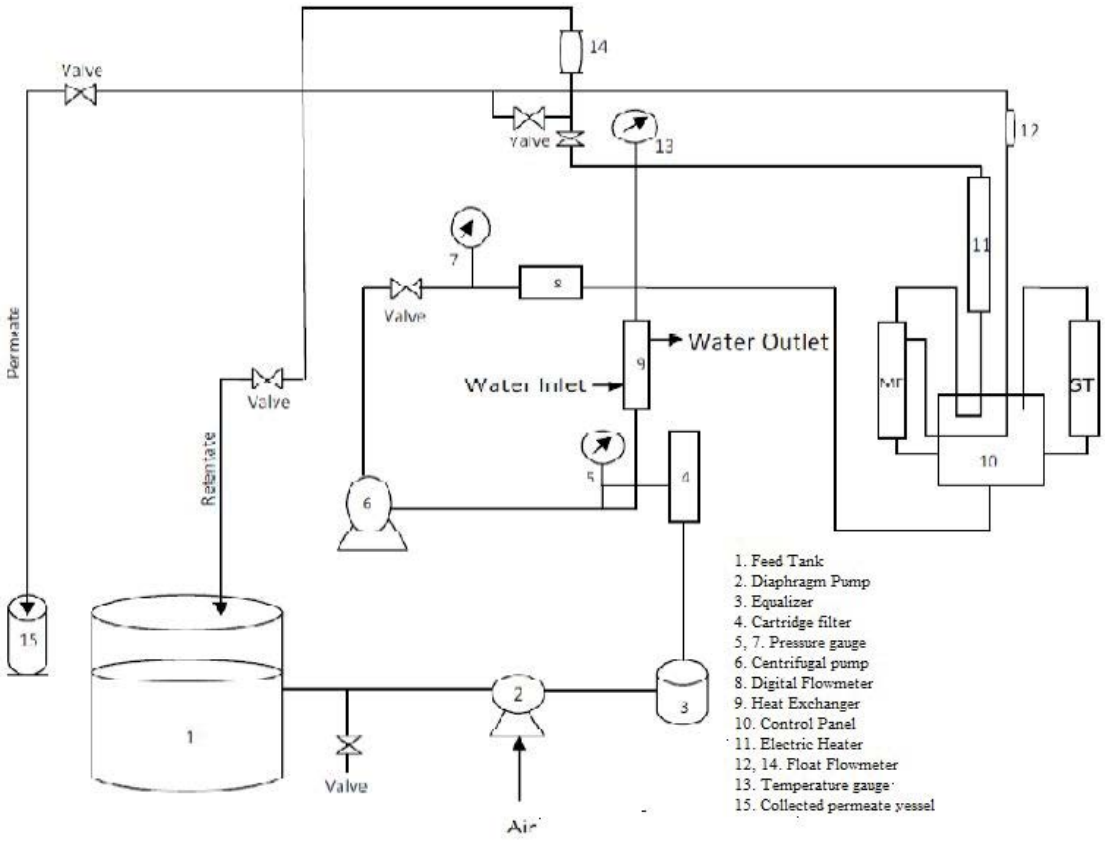

Fig. 1 Flow sheet of the MF pilot unit.

- Total suspended solids (TSS) were determined by vacuum filtration of sampling using tared crucibles with 0.45 µm whatman filter paper.
- Turbidity tests were performed using a turbidimeter (Model 43900, Hach Co., Ames, IA)
- UV-vis absorbance using Hewlatt Packard diode array spectrophotometer (model 8451A). The UV-vis spectrophotometric data were used to notice trends on organics removal or accumulation, based on the comparison of absorption intensities for raw, permeate and retenate water samples at wavelength (254 nm) representing an abundance of dissolved organic matter contents, The optical quality of NC samples is determined by three successive measurements of the light absorption in a spectrometer (Quinchon and Tranchant, 1989): at 460 nm where the optical density is the sum of the coloration and turbidity. at 630 nm where the optical density is only related to the turbidity.
- Total dissolved solids (TDS) through fiber filter GF/C 47 mm,dried in oven at 180°C.
- Total organic carbon (TOC) using total organic analyzer (Dohrman, model DC-190)
- Chemical oxygen demand (COD) is measured chemically using $K_2Cr_2O_7$.
- Conductivity using a Radiometer CDM92 model
- Turbidity using LaMotte 2020 turbidimeter (La Motte, Chestertown, MA, USA)
- Viscosity using Brookfield DV-I viscometer.
- The pH value was determined using a microprocessor pH meter HANNA model HI-9321.

Characterization of NC and membranes

The skin layer structure and cross sections of virgin and fouled MF membrane were determined using scanning electron microscope (SEM). TEM image analysis was performed to obtain the particle size distribution of NC fines using scanning/ transmission electron microscopes (models 6300/ JEM-2010, JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

Characterization of NC samples

Analysis of the two NC wastewater types (A and B) are shown in Table 2 in which, sample (A) is characterized by higher values of the tested parameters compared to sample (B). (Fig. 2) manifests the TEM image analysis of both types of NC fines (A

Table 2. Analysis of two different types of NC wastewater samples (A&B).

Item	TSS	TDS	NC	COD	TOC	Turbidity	Conductivity	UV-absorbance		
	mg/L					NTU	µs/cm	254	460	630
Sample (A)*	432	735	432	519	340	452	840	2.5	2.19	2.08
Sample (B)#	318	342	318	457	257	325	360	1.6	1.8	1.723

* NC Civilian grade
#NC Military grade

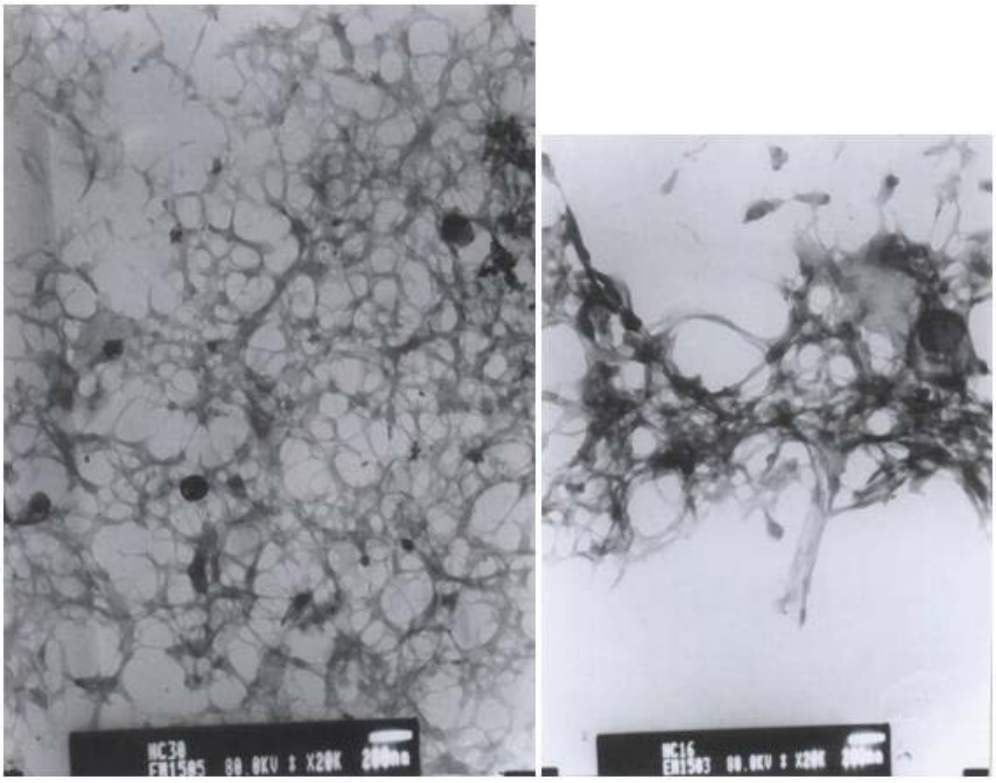

Fig. 2A and 2B TEM picture of NC samples.

and B). The particle size analysis with sample (A) is from sub micrometer to several hundred micrometer while, sample (B) is greater than several hundred micrometers in length

NC synthetic wastewater using MF

Effect of TMP: (Fig. 3 and 4) show the flux decline with TMP during 30 minutes for NC samples (A and B), respectively. The result indicates that the increase in TMPs led to an increase in both initial and final flux values in both types. Significant reductions in flux for the first 20 min and 15 min for samples A and B, respectively indicates the higher tendency for fouling for sample B than sample C. At TMP=2 bar, the permeate flux is decreased from 120 to 60 L/m^2.h and from 105 to 55 L/m^2.h for samples A and B, respectively. This observation is consistent with (Mikulašek, *et al*., 2004; Byung, *et al*., 1997) findings which concluded that the flux decline was due to cake build-up while (Balakrishnan, *et al*., 2000) demonstrated that the significant flux decline was due to the deposition of small particles and colloidal on the membrane surface which led to the membrane fouling. The steady-state flux was obtained implying that the fouling layer was almost established after 30 min.

After steady state, it is observed that for NC (A and B), shear forces are sufficient to minimize particle deposition and the flux is proportional to the applied pressure at low pressures (less than 1 bar). Further increases in pressure accelerate the accumulation of particles on membrane surface without a corresponding increase in flux reaching a limiting flux at 1 bar as shown in (Fig. 5 and 6).

Further, the effect of TMP decrease indicates some loss of the effective flux which is attributed to the presence of persistent adsorbed layer of fines on membrane surface. Thus, the deposited organic fines comprise two components, the first is quickly

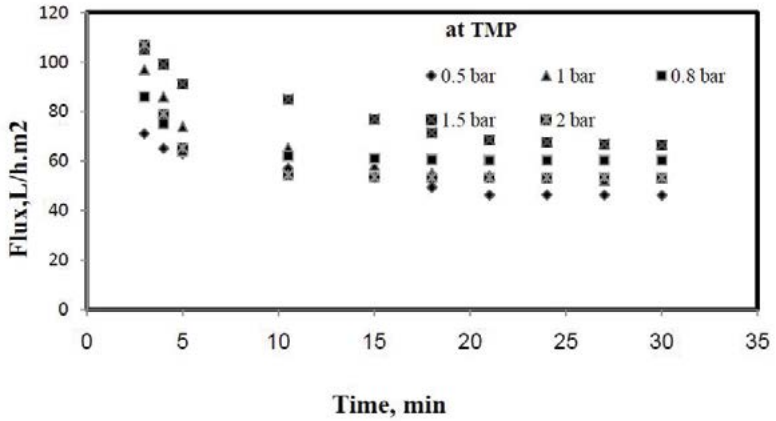

Fig. 3 Effect of TMP on MF flux decline (Vc= 1 m/s, NC (A) =200 mg/l, T=20°C).

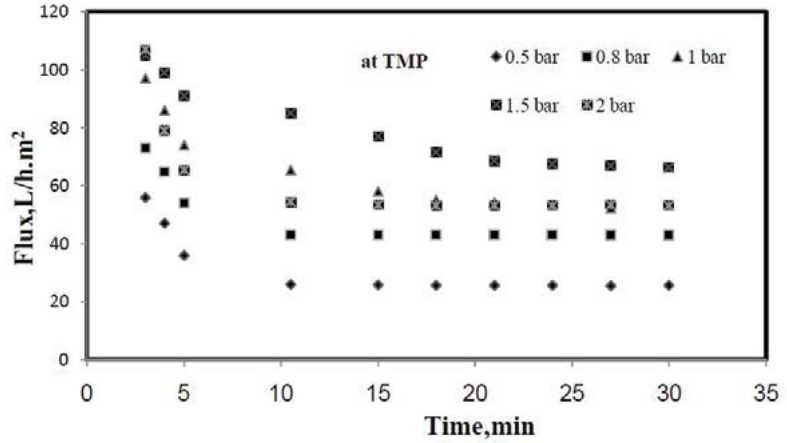

Fig. 4 Effect of TMP on MF flux decline (Vc= 1 m/s, NC (B) =200 mg/l , T=20°C).

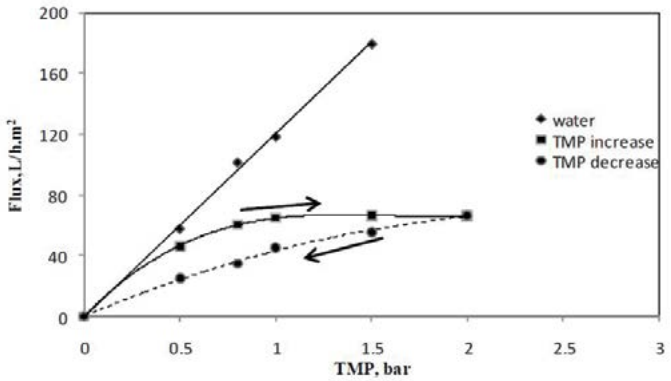

Fig. 5 Effect of TMP increase and decrease on MF flux after steady state (Vc=3 m/s, NC (A) =200 mg/l , T=20°C).

removed by increasing TMP and membrane cleaning while, the second component may be strongly adhered to the membrane surface and required more drastic chemical cleaning. The area between the two lines representing the forward TMP increase and the reverse decrease indicates hysteresis phenomena associated with partial flux loss.

Hysteresis equations manifesting flux values as a function of pressure in the forward and reverse directions for MF (NC type (A)) are described respectively as follows:

Flux=17.64 P3 - 84.5P2 + 131.7P R2=0.999

Flux=2.287 P3 - 17.03P2 + 58.06P R2=0.997

Hysteresis equations for NC type(B) are as follows

Flux=-0.292 P^3 -21.65 P^2 + 71.22P R^2=0.982

Flux= -12.53 P^3 + 29.97 P^2 + 16.86P R^2=0.99

Further, the area under the curve represents the magnitude of hysteresis for MF using NCA and B are 28.6 and 20.01 L/m^2.h.bar, respectively.

Effect of membrane cleaning

The effect of membrane cleaning is illustrated in (Fig. 7 and 8). The membrane flux has been improved due to combined effect of washing and increasing the TMP up to 2 bars. Decreasing the pressure indicates decrease of steady state permeate flux. The effect of cleaning seems mandatory for sustainable membrane performance types (A) and (B). The increase in cross flow velocity leads to higher final flux. A significant flux decline can be observed clearly where the reduction percentage is within 40-50%. A rapid flux decline observed in carbo-sep membrane was within less than 10 min and later a plateau was reached (Fig. 9 and 10).

Flux decline behavior is represented by the following correlations:

MF/NC (A) J=78.5(TMP) 0.26 x v0.36 + e-0.00088t R2=0.88

MF/NC (B) J=75(TMP) 0.4 x v0.3 + e-0.016t R2=0.81

Effect of NC concentration

(Fig. 11) shows the influence of the two types of NC (A) and (B) concentrations with steady state flux under operating conditions of 1 bars and cross-flow velocity of 3 m/s. The increase in NC concentration leads to sharp decrease in flux

Batch concentration of NC

In batch concentration mode in which, permeate is collected separately and concentrate is recycled to the feed tank, (Fig. 12) showed that the permeate flux decreased gradually with time by increasing the volume reduction factor (VRF) defined as the ratio between the initial feed to the resulting concentrate volumes). The initial permeate fluxes are 114 and 96 L/h.m^2 for NC (A) and NC (B), respectively when VRF values reached 6 folds. The flux vs. VRF curve is characterized by a rapid decrease of flux till VRF= 1.5 then, a lower decrease of flux

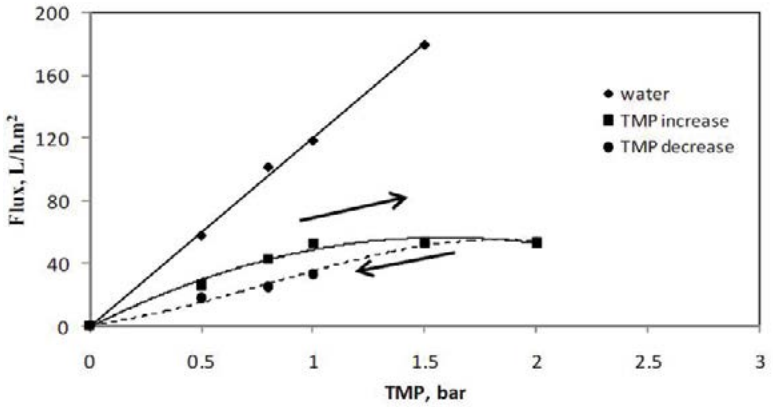

Fig. 6 Effect of TMP increase and decrease on MF flux after steady state (Vc=3 m/s, NC (B) =200 mg/l , T=20°C).

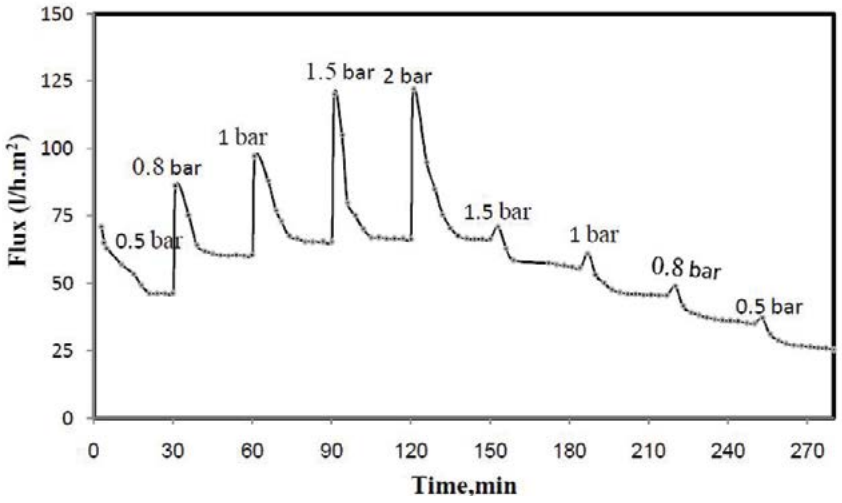

Fig. 7 Effect of TMP on MF flux decline (Vc= 1 m/s, NC (A) =200 mg/l, T=20°C).

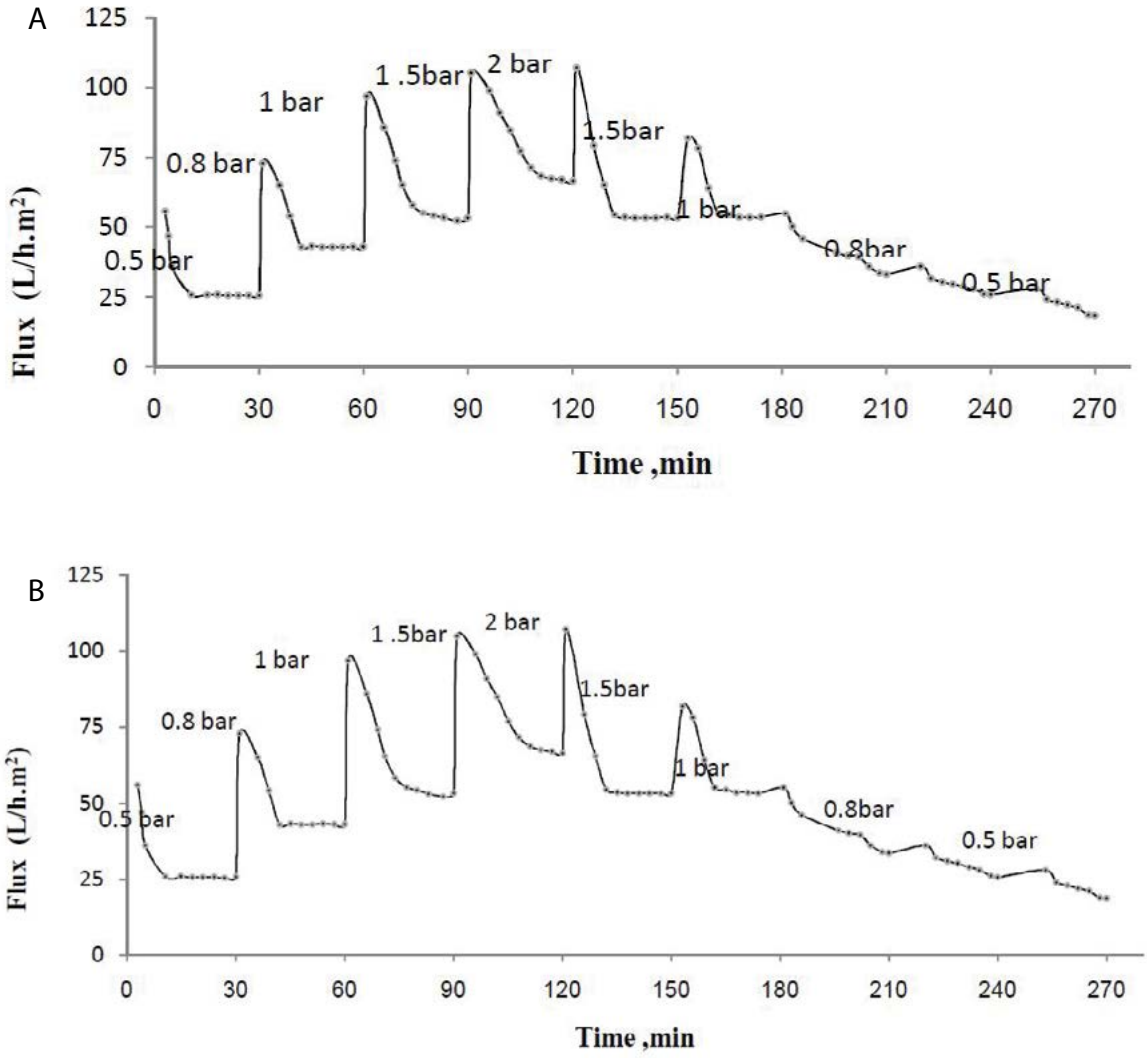

Fig. 8A and 8B Effect of TMP on MF flux decline (Vc= 1 m/s, NC (B) =200 mg/l , T=20°C).

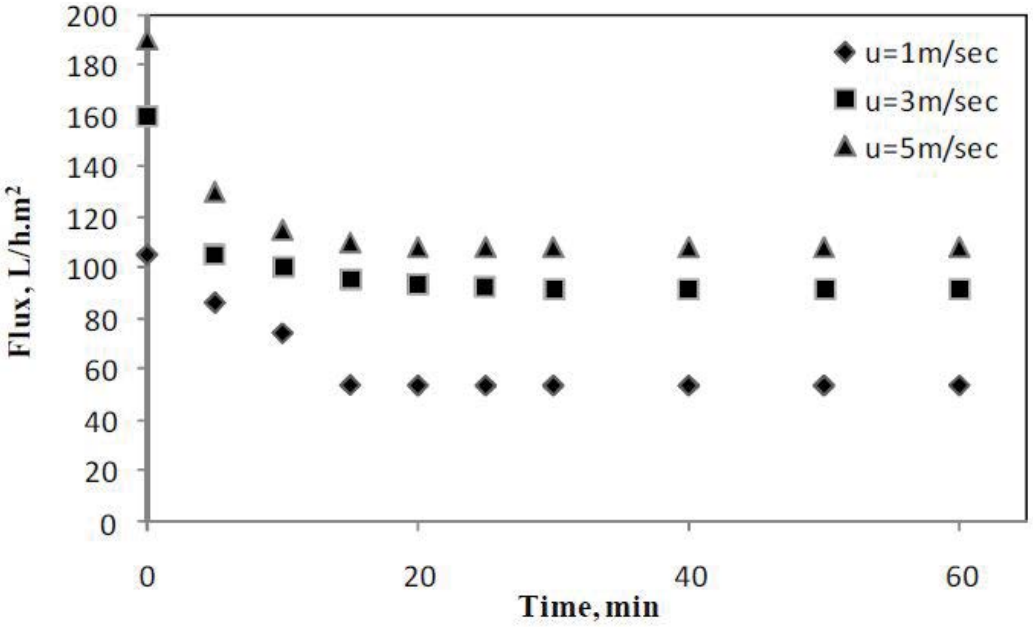

Fig. 9 Effect of cross -flow velocity on MF flux (TMP= 1bar, NC(A)= 200 g/l and T=20°C).

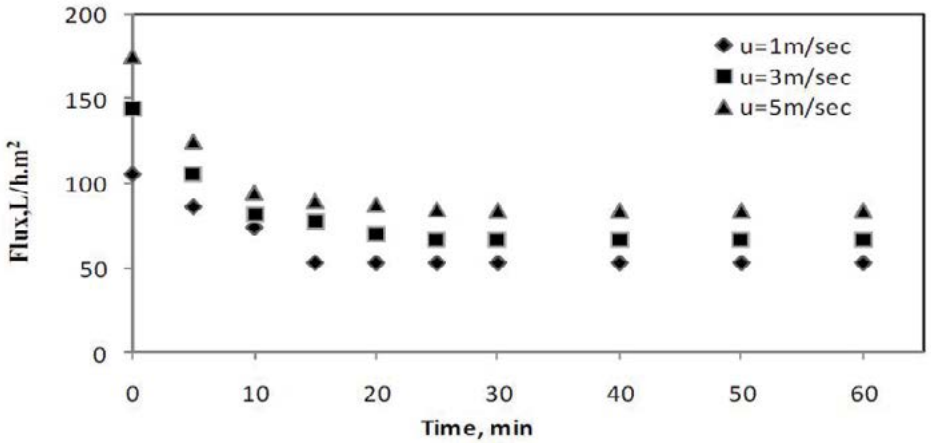

Fig. 10 Effect of cross -flow velocity on MF flux (TMP= 1bar, NC(B)= 200 g/l and T=20°C).

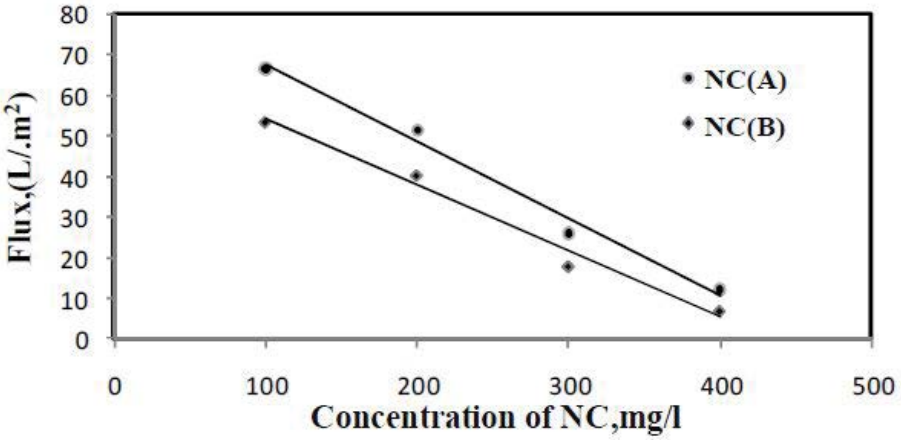

Fig. 11 Effect of NC concentration on MF flux (TMP= 1 bar, Vc=3 m/s and T= 20°C).

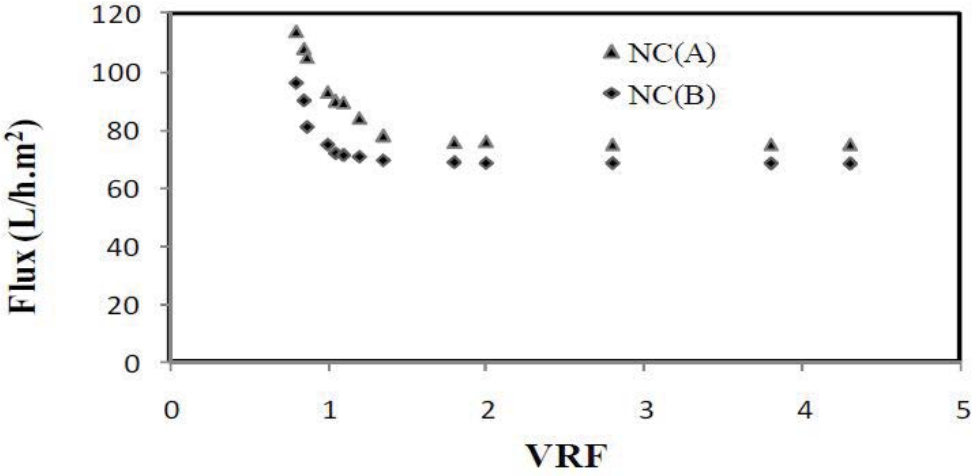

Fig. 12 Effect of VRF on MF flux (TMP= 1 bar, Vc=3 m/s and T=20°C).

MF permeate quality of NC synthetic

TSS rejection of 96.2-98.7% and 94-97.3% for NC (A) and (B), respectively is obtained at all the tested TMP and Vc giving a value ranging from of 0–3 mg/L for the permeate side. Turbidity is decreased of 95.4% -98.3% and 93% -97.8%, respectively.

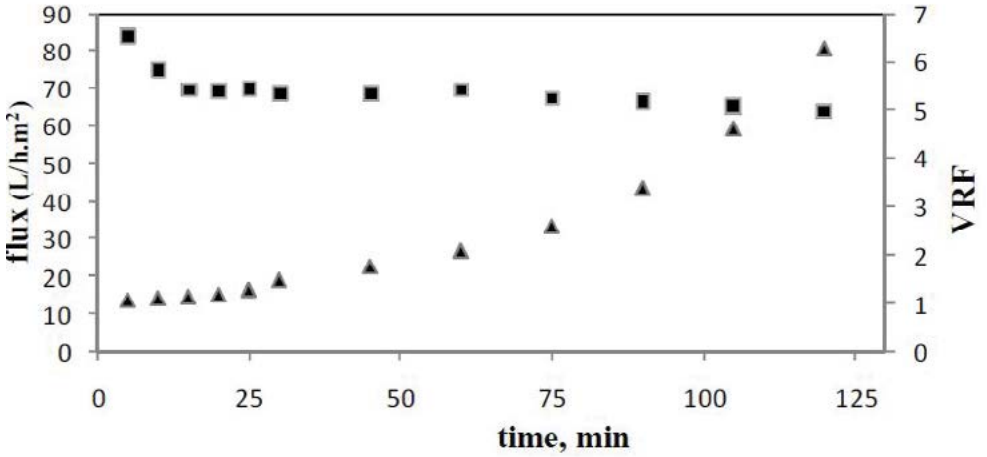

Fig. 13 Time course of permeate flux and VRF (TMP= 1 bar, Vc=3 m/s and T=20°C).

NC real wastewater using MF

Sample from real effluent wastewater NC(A)was treated with MF membrane to evaluate the efficiency of MF membrane at optimum conditions: (TMP=1 bar, Vc=3 m/s and temperature 20 ± 1°C) that based on the best results obtained during experiments of separation and concentrations of synthetic solution of NC fine using MF. We select only NC(A) in this study because MF filtrate through 0.45 µm filter paper with yellow color is suspected to have a significant amount of dissolved organic matter which causes foulants in addition to colloidal NC. While as the NC (B) was excluded because it has no significant amount of dissolved organic matter.

Batch concentration mode of MF experiments on NC real wastewater

In concentration mode, in which the permeate stream was continuously collected during filtration and in recycle mode, in which permeate, and concentrate were remixed in the feed tank. The results showed that the permeate flux decreased gradually with the operating times by increasing the volume reduction factor (VRF) (Fig. 13) due to concentration polarization and cake formation. The initial permeates flux of 84 L/h.m^2 to about 64 l/h.m^2 when the VRF value reached 6.23.

MF Permeate quality of NC real wastewater

Results analysis of collected permeates of MF membrane for real wastewater of NC(A) shows that there is a very small variance, UV absorbance at 254 nm, TOC and COD with initial values of feed sample while the percentage rejection R (%) values of TSS and turbidity, UV absorbance at 460 nm and at 630 nm are 98.9, 99.6, 95.9 and 93.7 respectively. these results confirmed that organic matter which is present in real wastewater NC(A) is not foulant MF membrane with NC fines. Fouling observation of MF membrane which fouled after filtration of the NC(A) real wastewater sample at operating conditions: Δp, 1 bar, cross-flow velocity, 3 m/s and temperature 20 ± 1°C) was examined by SEM. (Fig. 13) shows virgin MF membrane (A) and fouled membrane (B). It can be seen that the cake layer is composed of densely packed debris of NC fines as shown in (Fig. 13). The same observation was finding with (Byung, *et al*., 1997).

CONCLUSIONS

A pilot-scale microfiltration and nanoflitration (MF/ NF) filtration system was constructed to study the feasibility of NC recovery from the industrial wastewater generated from NC manufacture process. Batch concentration mode experiments were performed on the synthetic and real wastewater at different operating parameters.

The scanning electron microscope (SEM) for both the original and used membranes showed that the MF membrane was fouled only by NC fines the MF/ NF process, allowed the recovery of NC fine from industrial wastewater and reuse more than 80% of the original wastewater. The quality of NF permeates obtained at trans membrane pressure of 5 bar and crossflow velocity 7 m/s showed low values of salts: 300 mg/L, conductivity: 290 µS/cm, COD less than 5 mg/L. and non-detected TOC.

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