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Ceramic Membrane Coating with Graphene Oxide for Tannery Wastewater Treatment

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***Abstract*—** Treatment of tannery wastewater produced from an ingeniously leather industry was carried out using a ceramic membrane coated with graphene oxide. The effluent was highly contaminated and thus posed a great threat to the terrestrial and aquatic life by polluting the environment. The current study proposed treatment of aforementioned wastewater with graphene oxide coated ceramic membrane. Graphene Oxide, synthesized by Modified Hummer's method, was coated on the inner surface of tubular ceramic membrane with a suspension of 5 mg/ml using dip-coating technique. Experiments were performed at different transmembrane pressures ranging from 0.7 bar to 3 bar while keeping the temperature and crossflow velocity constant. Rejection values for total solids, total dissolved solids, total suspended solids, salinity and conductivity were determined to evaluate the efficiency of the coated membrane.

***Keywords*—** Ultrafiltration, tannery wastewater treatment, ceramic membrane, Graphene Oxide, dip-coating.

I. INTRODUCTION

A major threat with increasing industrialization is the discharge of huge quantity of wastewater polluted with dyes. These wastewaters containing many toxic chemicals become part of streams, canals, rivers and seas, thus polluting the environment [1, 2]. Two types of industries including textile and dye manufacturing industries are contributing majorly in this regard. The wastewater coming out of these industries contain a large quantity of carcinogenic and toxic chemical additives. The reason is that these dyes are made-up of chemical such as benzidine and other aromatic compounds, which are carcinogenic in nature and may be reformed due to microbial metabolism. Among these, azo and nitro compounds has the ability to reduce in sediments and intestinal environment, resulting in reformation of toxic amines [3]. For this purpose, the treatment of such wastewater is of the primary concern to minimize the problems arising from the prescribed industries.

Among all the processes available for water treatment, membrane filtration is rated to be the most economical and efficient one. Membrane filtration is relatively a simple process and requires less energy [4-6].

Selection of membrane in this process is one of the most important steps that defines stability and viability of the process. Of all the different types of membranes, polymeric and ceramic membranes are used more commonly. Polymeric membranes have more flexibility, easier preparation process and less costly, but these membranes have some disadvantages including fouling, poor chemical and thermal resistance and short lifespans. On the other hand, inorganic ceramic membranes have higher strength, thermal stability, chemical resistance, and long lifetime. Their drawbacks include high costs, complex preparation methods and brittleness. An ideal membrane will be the one having both the desired properties of polymeric and ceramic membrane [7, 8].

The discovery of carbon nanotubes (CNTs) created the possibilities of achieving ideal membranes as they have flexibility like polymeric and stability like ceramic membrane [9]. Some theoretical studies were carried out which were in favor of using these 1-D tubes in water treatment, but the complications in preparation of CNT based membranes and their high costs diminished researcher interests in these tubes [10, 11]. Besides, the oxidized form of graphene, known as graphene oxide (GO), has attracted scientists due to its tremendous properties [12, 13]. GO is a well-emerged two dimensional material with O functional groups decorating the sp2 C basal plane. The presence of O functional group makes GO hydrophilic due to which it can be dispersed in water, contrary to graphene which is hydrophobic. The size of the GO flakes can be also tuned and varied from a few nm to mm. The tunability of both its chemical composition and flakes size makes GO an appealing material in many fields: electronics (sensors and transparent conductive films), composites materials, clean energy devices, biology, medicine and watertreatment[14]. In the present work, tubular ceramic membrane has been coated with a suspension of 5 mg/ml using dip-coating technique for wastewater treatment.

II. MATERIALS AND METHODS

A. Microfiltration Ceramic Membrane

The membrane used in this work was imported from Toho Ceramic Technology Co., Ltd, China. Table 1 shows characteristics of membrane used for coating purpose.

TABLE 1: CHARACTERISTICS OF CERAMIC MEMBRANE USED FOR GO COATING

Parameter	Value
Length	250 mm
Outer Diameter	10 mm
Internal Diameter	06 mm
Thickness of membrane	04 mm
Surface Area (internal)	47.7 cm2
Surface Area (external)	80.1 cm2
Pore size	50 nm
Membrane Type	TOHO01*10
Membrane Material	Alumina Ceramic

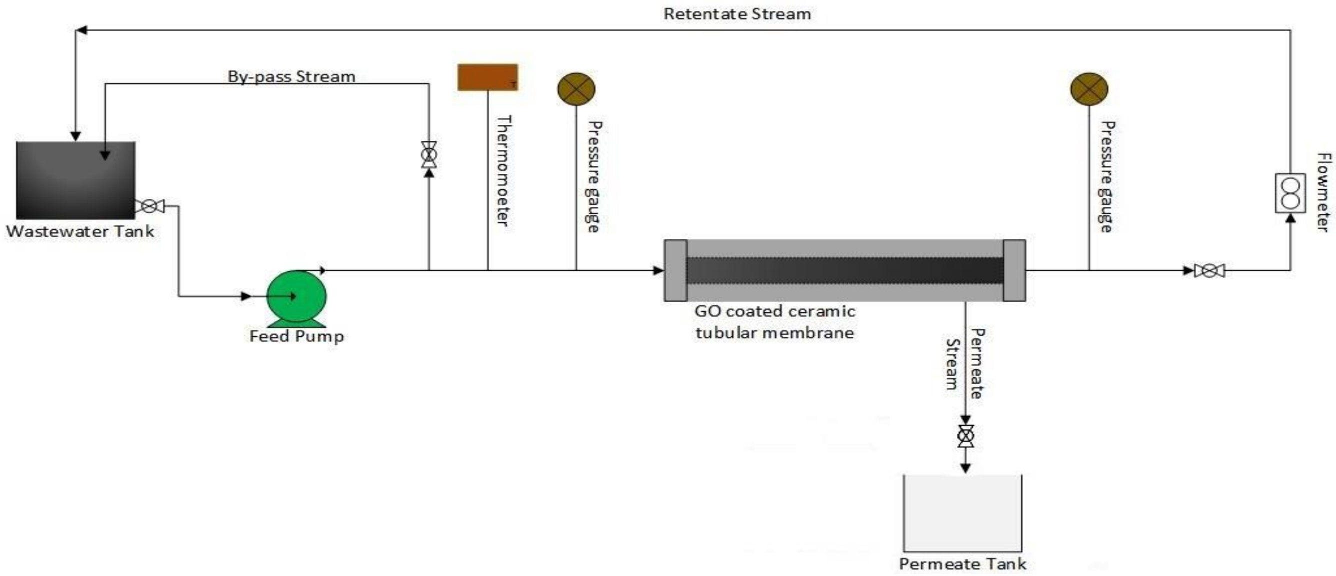

Figure 1: Cross-flow Tubular Membrane Filtration Unit

B. Ceramic Membrane Coating with Graphene Oxide

Graphene oxide was synthesized by Modified Hummer's method [15]. Following that, 5 mg/ml suspension of GO was prepared by mixing 0.5 g of GO powder in deionized water to make 100 ml of suspension. The suspension was then subjected to sonication for 30 minutes to make a homogenous and stable dispersion of GO nanosheets [16]. Following that, a thin layer of GO was coated over the surface of ceramic membrane using dip coating technique. For this purpose, the ceramic membrane was soaked in water for 2 hours to saturate the pores with water. Then the membrane coating was done in such a way that outer side of the membrane was covered with aluminum foil while GO dispersion was poured inside the tube. The GO dispersion was let for 10 minutes inside the membrane to form a uniform layer on ceramic membrane. The membrane was then subjected to heating at 100^{o}C in furnace for strengthening of the covalent bonds between GO and the ceramic membrane [17].

C. Cross-Flow Membrane Filtration Unit

The experiments were performed on a lab scale cross-flow membrane unit, the diagram of which is shown in figure 1. A diaphragm pump with a capacity of 1.8 L/min was used to circulate the effluent though the unit. A thermometer, flowmeter and two pressure guages were installed to measure the temperature, flowrate and pressures respectively. The crossflow velocities and transmembrane pressure were adjusted through the flow control valves installed on the main stream and by-pass stream. A stainless steel tubular membrane pressure vessel was present for holding the membrane.

All the experiments were carried out under total recycle mode with both the retentate and permeate returning to the feed tank. Permeate samples were collected after every 5 minutes for one hour. The flux and rejection was calculated using the equations (i) and (ii) respectively:

$$J = \frac{Q}{A \times t} \qquad \text{(i)}$$

$$R\% = \frac{C_f - C_p}{C_f} \times 100\% \qquad \text{(ii)}$$

Where,
J is the permeate flux,
Q is the permeate flowrate,
t is the time taken by each experiment,
A is the effective membrane area,
R% is the rejection percentage,
C_f and C_p is the concentration of feed and permeate respectively [**Error! Reference source not found.**

III. RESULTS AND DISCUSSIONS

A. Membrane Permeability Test

Membrane permeability tests were performed at constant temperature of 25°C, constant feed flux of 1 L/min and different transmembrane pressures ranging from 0.2 to 3 bar. From Figure 2, it can be seen that water flux approximately takes 30 minutes to get stabilized.

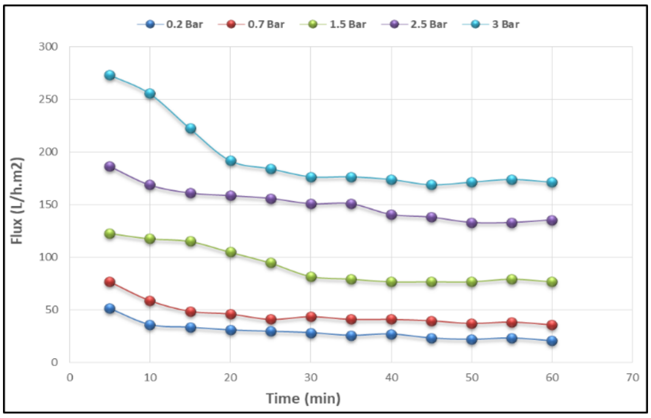

Figure 2: Deionized water flux vs operating time

It can also be observed that the water flux through the membrane is heavily depended upon the applied pressure and shows a linear relation with the transmembrane pressure. As shown in Figure 3, the value of membrane permeability using deionized water was noted to be 63.029 L/hr.m^2.bar.

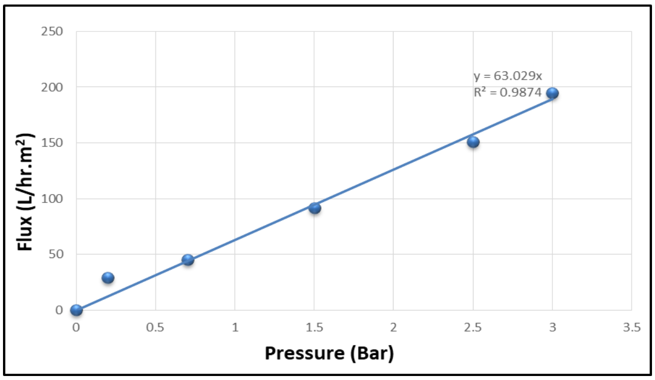

Figure 3: Deionized water flux variation with pressure

B. Effluent Properties

A sample of wastewater was collected from a locally situated dyes industry in Lahore. The characteristics of the collected effluent is given in table 2.

TABLE 2: EFFLUENT PROPERTIES

Effluent Property	Amount
Chemical Name	Acid Black 234
Chemical Formula	$C_{34}H_{26}N_{10}Na_2O_9S_3$
Molecular Weight	860.81
Total Dissolved Solids (TDS)	47.0 g/L
Total Suspneded Solids (TSS)	30 g/L
Total Solids (TS)	77 g/L
pH	8.8
Color	Brownish black
Conductivity	72 mS
Salinity	62.6 ppt

C. Effluent Permeate Flux

Experiments were performed using the GO coated ceramic membrane for dyes industries wastewater at room temperature i.e. 25°C, constant feed flowrate of 1 L/min and different transmembrane pressures i.e. 0.7, 1.5, 2.5 and 3 bar. Each experiment was performed for 65 minutes which were enough to reach the steady state. Permeate flux was monitored continuously and collected to find out its characteristics.

From Figure 4, it can be observed that the flux was high initially but then showed a sudden decline. This decline in flux can be associated to concentration polarization, which is the build-up of the solute particles near the membrane surface resisting the passage of solvent through the membrane.

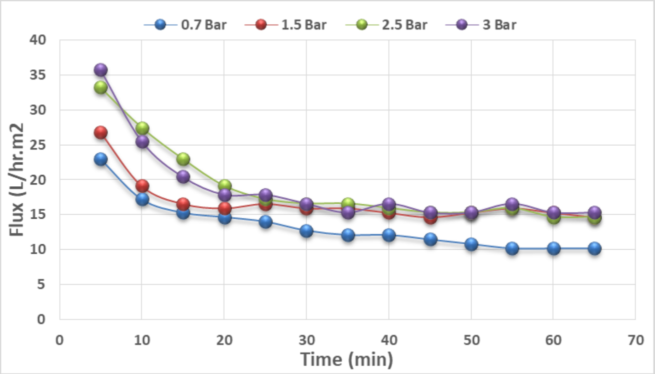

Figure 4: Effluent permeate flux vs operating time

Figure 5 shows that the flux increases exponentially by increasing transmembrane pressure till 2.5 bar, where it reaches its limiting value known as the limiting flux. Behind this pressure, the flux slightly decreased as a consequence of membrane compaction. The phenomena of membrane compaction does not usually occur in ceramic membrane, but the presence of GO layers made it applicable here. GO layers has the trait of getting compact at higher pressures and this was the main reason of flux decline over 2.5 bar [20].

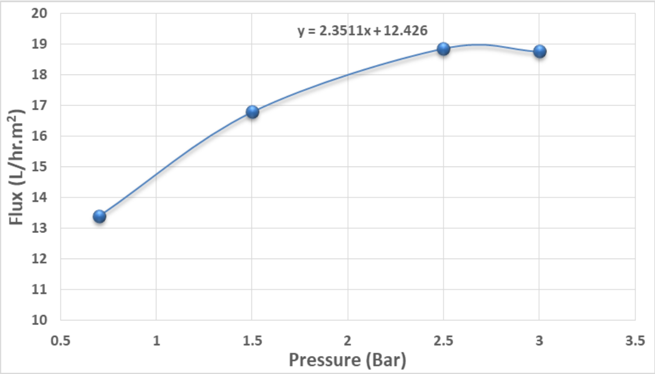

Figure 5: Variation of permeate flux with pressure

The average permeate flux of the membrane for dyes industries wastewater is noted to be 2.35 L/hr.m^2, which is very low in comparison with the one obtained for deionized water, hence confirms the polluting properties of the wastewater.

TABLE 3: MEMBRANE REJECTION PERFORMANCE AS AN EFFECT OF TRANSMEMBRANE PRESSURE

Effluent characteristics	**0.7 bar**	**1.5 bar**	**2.5 bar**	**3.0 bar**
Flux (L/hr.m^2)	13.40	16.79	18.85	18.76
TDS Rejection % (g/L)	82.69	80.34	79.62	80.05
TSS Rejection % (g/L)	92.78	91.07	89.16	92.24
TS Rejection % (g/L)	85.95	83.80	82.70	83.98
Conductivity Rejection % (mS)	83.90	81.55	80.83	81.26
Salinity Rejection % (ppt)	85.70	83.35	82.63	83.06

Table 3 shows the relationship between membrane rejection performance and transmembrane pressure. The percentage removal of different feed characteristics i.e. TDS, TSS, TS, conductivity and salinity are shown as an effect of the transmembrane pressure. For instance, TDS rejection has been maximum at 0.7 bar and shows a decreasing trend till membrane compaction at 2.5 bar. Membrane compaction narrows down the path for the particles due to which rejection increases and this has been observed in this case too. A reasonable rejection values are obtained for all parameters.

CONCLUSIONS

GO was synthesized through Modified Hummer's method. It was then coated on the inside of a ceramic membrane to enhance its separation ability. Water permeation tests under different transmembrane pressures were performed to find the permeability of the modified membrane. Finally, effluent permeate tests were carried out to find out the permeate flux and rejection. A limiting flux of 18.85 L/hr.m^2 was obtained at 2.5 bar. The membrane provided satisfactory results for the treatment of the effluent taken from dyes industry. These results can further be improved by optimizing GO layer thickness over ceramic membrane.

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