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Membrane Filtration from sludge as an Alternative Method for Wastewater Treatment

Rasha A. SaryEl-deen[1], Maha M. El-shafei [1], and Shakinaze T. El-Sheltawy[2], Rasha A. SaryEl-deen[1]

[1]Sanitary and Environmental Institute, Housing and Building National Research Centre, Giza, Egypt.
[2]Department of Chemical Engineering, Faculty of Engineering, Cairo University, Giza, Egypt.

Abstract : The study highlighted the ability of modified sewage sludge ash from wastewater based membranes were prepared by blending cellulose acetate (CA) with sewage sludge ash by dry-wet phase inversion method in various compositions of CA \SSA (100/0, 90/10, 80/20 and 50/50 % wt) and the effects of organic additives concentration as poly ethylene glycol (PEG600) in the casting solution range from (0-10) % wt, results in more added of PEG600 increase pore of membrane, using DMF as solvent. The membranes were characterized in terms of water content, XRD analysis and mechanical strength of blend membrane, evaluate solute rejection of nickel ions from wastewater. Best results were obtained for CA\SSA blend membranes at 50/50 wt%. Determination of membrane rejection was performed by reduction of water turbidity, the concentration of COD, BOD, TSS, and TDS from effluent wastewater from Abo-Rawash plant as case study before and after passing through the membrane.
Keywords : Blend membrane, Cellulose acetate\Sewage sludge as (CA\SSA), Nickel ions, and Phase inversion method.

Introduction

One of the most common applications for the membrane separation process is for water treatment to remove, concentrate or separate various components with different sizes such as particles, colloids, bacteria, viruses, proteins, humic matters, organic compounds, soluble salts, heavy metal ions and detergents [1,2]. Among these components, heavy metal ions such as Hg^{2+}, Cd^{2+}, and Ni^{2+} are highly toxic to human bodies even at very low concentration [3], therefore, removal of them is more crucial [4]

Some of the conventional membrane separation processes such as microfiltration (MF) and ultrafiltration (UF) cannot remove them because of the relatively larger pore sizes of the membrane (>50nm). In contrast, nanofiltration (NF) and reverse osmosis (RO) processes are generally not economical because of the high operating pressures (5-80bar) [5].

It is always desirable to be able to remove heavy metal ions with membranes of larger pores hence high permeate fluxes and low energy consumption [6,7]

To achieve high removal efficiency and high selectivity, this may be accomplished by using microporous adsorptive membranes that separate the desired or undesired substances from solutions through affinity adsorption, rather than size exclusion, sorption-diffusion, or ion exchange principles. When the feed is made to pass through the membrane thickness, the desired components to be removed or separated will interact with the functional groups on the external and internal surfaces while the liquid or other components that have low affinity for the membranes will pass through the membrane freely, and most of the commercial polymeric membranes are prepared by phase inversion technique[8].

Phase inversion technique is a common technique and a well-known method in producing asymmetric membranes [9]. The main important component in membrane preparation via phase inversion process is the polymeric materials, which determine the characteristics and properties of the produced membranes.

Some of these polymeric materials such as cellulosic's (e.g. cellulose acetate, cellulose nitrate), polyacrylonitrile and related block-copolymers, polysulfone/polyetehersulfone/ sulfonated polysulfone/ sulfonated poly (ether-ethersulfone), polyvinylidene fluoride, polyimide/polyetherimide, aliphatic polyamides, polyether ketone and sulfonated poly (ether–ether-ketone) are used as a back-bone of ultrafiltration membrane[10].

The selection of polymer material as a polymer back-bone to prepare an adsorptive membrane via phase inversion process is very crucial due to 1) membrane surface, 2) cost in production3) thermal and chemical stability 4) fouling and 5) mechanical strength . Generally, these properties are fundamentally related to chemical and physical nature of polymers.

Studied the effect of the varied additive on blend membranes from cellulose acetate/polyurethane membranes [11]. Investigated use of cellulose acetate was blended with sulfonated poly (ether ether ketone) in various compositions and subjected to various ultra filtrations[12]. Modified cellulose acetate based membranes were prepared in the absence and presence of polymeric additives such as polyvinylpyrolidone(PVP) and polyethylene glycol(PEG 600) in various compositions [13].

Cellulose acetate has been the most widely studied polymer for adsorptive membrane, the reactivity of cellulose comes from the hydroxyl groups (-OH) on the polymer backbones, [14] however, OH does not show the direct binding capability to heavy metal ions or proteins. It needs further derivation with other more reactive functional groups such as $–NH_2$, oxides, $-SO_3H$ and carbonaceous materials. Many research have been obtained to more reactive polymer to be blended with SSA to produce membrane with porosity, high carbons content material as activated carbon and an extended particulate surface area of the SSA [15].

The aim of the study prepared adsorptive membranes by blending cellulose acetate and sewage sludge ash with various compositions and their effect on water content, XRD and mechanical strength of the blend membranes are evaluated and compared with membranes made from pure cellulose acetate. The prepared membranes were tested for Ni removal from synthetic wastewater as well as actual sanitary wastewater obtained from Abo Rawash plant was investigated.

2. Materials and Experimental

2.1 Materials

Materials used in membranes preparation are cellulose acetate (CA) purchased from sigma Aldrich chemicals; sewage sludge waste (SSW) sample used in this study was collected from EL-Berka municipal wastewater treatment plant in the South of Egypt treatment. Acetic acid (glacial, 99-100%), Poly (ethylene glycol 600) was procured from Merck (I) Ltd., and used as a non-solvent additive, Annular grade N, N-dimethylformamide (DMF) and sodium lauryl sulfate (SLS) were obtained from Sigma company and subsequently used in the experiments in Housing and Building Research Center (HBRC).

2.2 Experimental

2.2.1 Preparation of SSA

The (SSW) sample was dewatered to sludge cake and burned in a modular incinerator at 600 °C for 2 h to provide incineration ash and then ground. The ground SSA was screened by 75 µm sieve [16].

2.2.2 Membrane preparation

The blend solutions based on CA and SSA (total polymer concentration = 20 wt%) were prepared by dissolving CA\SSA with different compositions of 100/0, 90\10, 80\20 and 50\50 wt% in the presence and absence of additive PEG600 (0–10 wt%) and dissolved in DMF (80 wt%) under constant mechanical stirring at 400 rpm for 1 h at 25±2 ◦C. The homogeneous solution that was obtained was allowed to stand at room temperature for 20 min in an airtight condition to get rid of air bubbles [17]**.**

Prior to casting, a 2 L gelation bath, consisting of 2.5% (v/v) DMF solvent (to reduce the rate of liquid–liquid demixing and macrovoids) and 0.2 wt% surfactant, SLS (to reduce surface tension at the polymer–non-solvent interface) in distilled water (non-solvent), was prepared and kept at 20±1 °C.

After 1–2 h of gelation, the membranes were removed from the gelation bath and washed thoroughly with distilled water to remove all DMF and surfactant from the membranes. The membrane sheets were subsequently stored in distilled water, containing 0.1% formalin solution to prevent microbial growth. [18]

2.2.3 Experimental setup

The ultra filtration experiments were carried out in a batch type, dead end cell (as shown in Fig. 1). This cell was connected to a compressor with a pressure control valve and gauge through a feed reservoir**.**

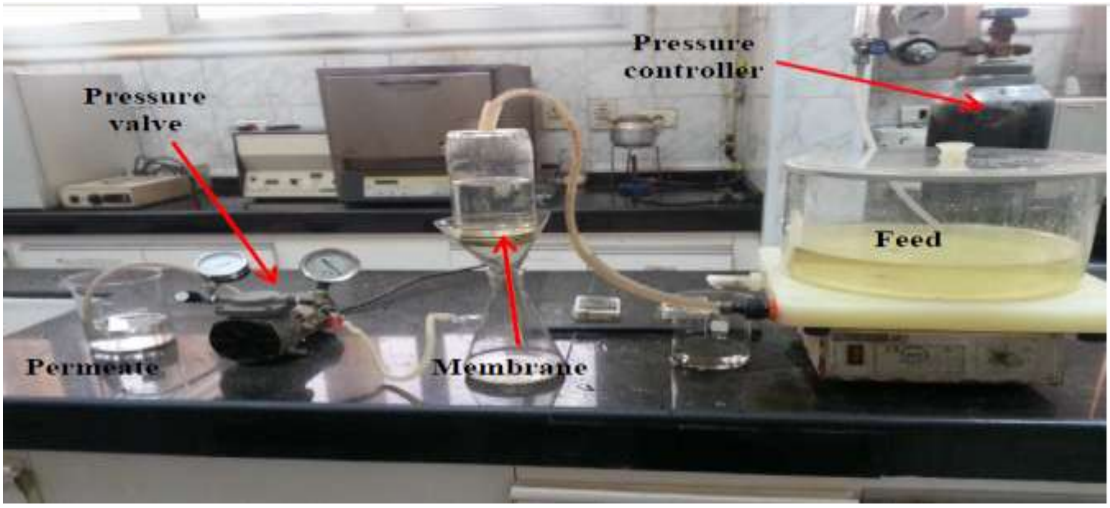

Figure (1) System Used in This Study

2. 2.4 Characterization of membranes

- **X –Ray diffraction analysis (XRD**)

Blending of CA\SSA was tested using XRD analyzer, after placing the samples in stainless steel sample holder, the XRD patterns were recorded at the radiation wavelength (Cu K-alpha = 1.5418 A°).The X-Ray current and voltage values were 40 kV and 40 mA, respectively. The diffraction angle (2θ) ranged from 5° to 50° at a step size of 0.0167° [19]**.**

- **Water content (WC)**

The water content of membrane samples was estimated by removing the membranes from water and weighing immediately after blotting the free surface water, and drying in oven for 1 h at 50°C. The percentage of water content of the membranes was calculated as below [20]

$$WC = \frac{W_w - W_d}{W_w} \times 100 \qquad (1)$$

Where:
Wc: water content (%).
W_d: dry weight of membrane (g).
W_w: wet weight of membrane (g).

- **Mechanical strength measurement**

The tensile stress, elongation ratio and young modulus values at break for the blending membranes CA/SSA/PEG are tested by Shmiduzue machine, model AG-X,100KN, Japan [21]. Young's modulus of the polymeric films was measured using a Shimadzu autograph in air at room temperature.

The correlation between stress (σ in M_{Pa}) and elongation (ε in %) was determined by Equation (2) [22].

$$\sigma = E\varepsilon \quad (2)$$

Where: E = Young's modulus in MPa,

ε= (Lo-L) / L

Where: Lo = original length L = length after elongation

2.2.5 Membrane testing for pollutants removal

Prepared membranes were tested for removal of nickel ions from synthetic wastewater and removal of COD, BOD, TSS, TDS, etc from Abo-Rawash wastewater treatment plant.

- **Preparation of synthetic solution**

According to Standard method for water and wastewater reported in (**ASTM 2005**).Nickel solution has been prepared and used in the laboratory experiment. The simulated stock of nickel ions (1000mg/L) was prepared by dissolving 4.47 g of an annular grade of respective salt in the 1L of distilled water. The salt used is Nickel sulfate $NiSO_4 .6H_2O$ .The stock solution was further diluted with distilled water to desired concentration of 25, 20, 10, 5 mg/L.

- **Sanitary wastewater**

Wastewater samples were collected from effluent Abo-Rawash wastewater treatment plant in Giza, Egypt .Table (1) shows physico-chemical analysis of wastewater sample.

Fill the synthetic wastewater with nickel ions in the system was introduced to the experimental set up above in figure (1) filtration permeate solutions of corresponding membranes were collected in 250 ml beaker and were analyzed for concentration of Nickel ions using atomic absorption spectrometer (ASS) (Model ICE 3000 Series - Thermo Scientific), with air acetylene flame at wave length of 231.6 nm. The percentage solute rejection (%SR) was calculated from the following equation:

$$\%SR= [1-(C_p-C_f)] \times 100 \quad (3)$$

Where C_p: Concentration of permeate, C_f: Concentration of feed

Then fill effluent wastewater from Abo-Rawash plant and determined of the pollutants according to ASTM (2005).

3 –Results and Discussion

Adsorptive membranes prepared from cellulose acetate blended with sewage sludge ash with various compositions (total polymer concentration 100 wt %) all shown in figure (2).

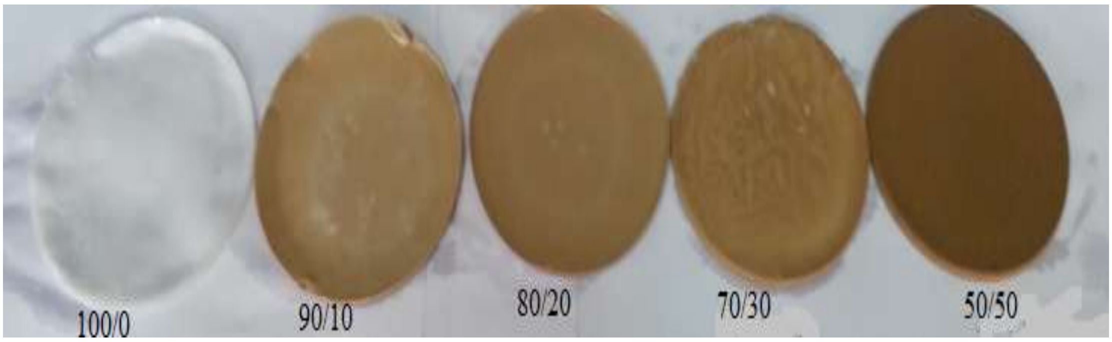

Figure (2) photo of CA\SSA blend membrane at various % wt

3.1 X –Ray Diffraction Analysis (XRD)

XRD studied were carried out to characterize different prepared membranes .results are illustrated in figure (3) from which it may be observed that cellulose acetate membrane is represented by the weak intensity peaks as 3.a which confirms its amorphous nature related to permeate flux ,while sewage sludge ash indicates major mineral phases in the specimens were calcite ($CaCO_3$), anhydrite ($CaSO_4$), cristoblite (SiO_2) and quartz percentage (SiO_2) (b) .Blending membrane CA\SSA at 50/50 wt% show the crystallinity of the prepared polymer blends (c) was observed that had three peaks at two diffraction angle of 2θ=13.06, 20.61 and 33.12° which crystallinity of membrane improve the % removal of nickel ions from wastewater .

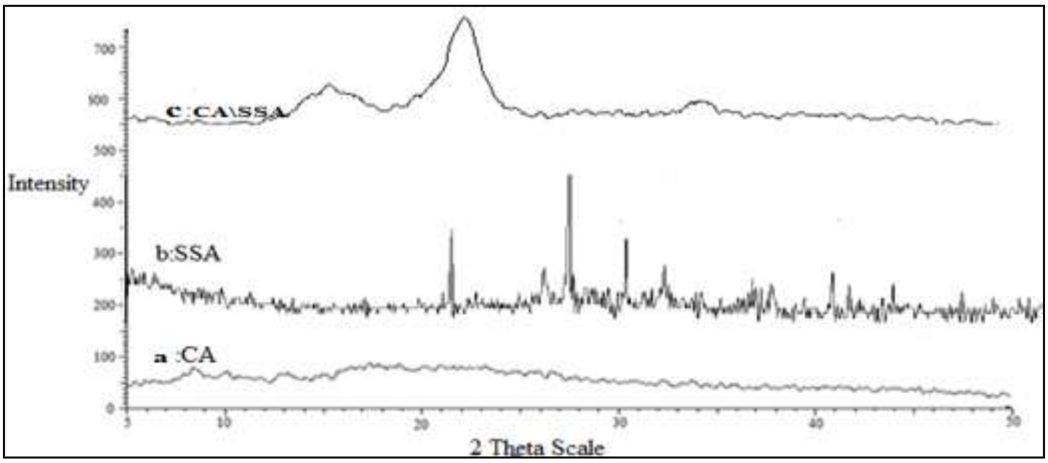

Figure (3) XRD diffraction of CA, SSA and CA\SSA

3.2 Water Content for Prepared Membrane

The influence of SSA content and PEG 600 concentration in the casting solution of CA\SSA at 100\0, 90\10, 80\20 and 50\50 wt % in solvent DMF (80 wt%) on WC are presented in figure (4), illustrated that WC increase wit PEG 600 concentration from 0-10 wt% and SSA content .this may be due to the fact that gelation was produced leading to formation of pores acting as domine of water molecules and since PEG 600 act as hydrophilic source for attracting water molecules inside the membrane blends.

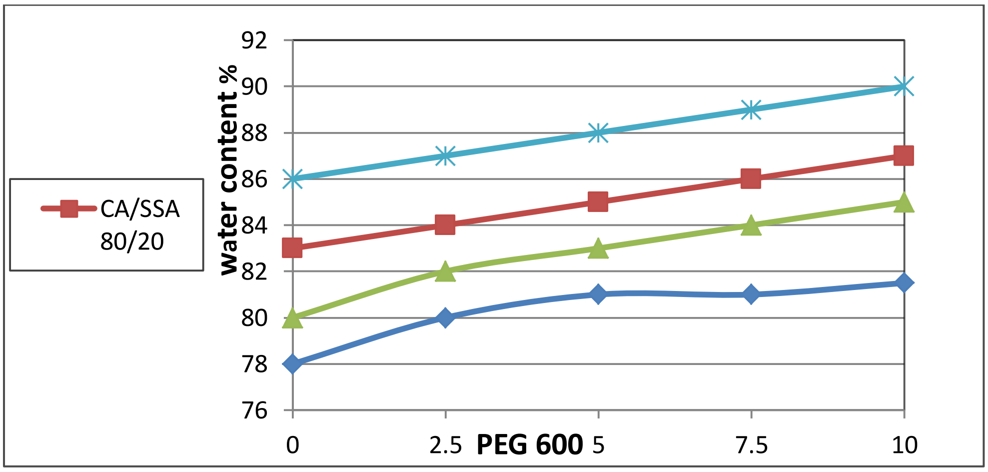

Figure (4) Effect of PEG600 on water content using CA\SSA blend membranes

3.3 Mechanical Strength of prepared membrane

The mechanical strength of each membrane was confirmed by measuring tensile modulus of membrane ,indicating that the tensile stress values of blend membranes from CA\SSA at 90/10, 80/20 and 50/50 wt% are 38.4 , 51.8 and 72.13 N\mm^2 respectively increased when SSA ratio increased indicate SSA in membrane improve the mechanical strength of blending membranes rather than used pure CA at 100/0 , having stress 32.5 N\mm^2.

3.4 Effect of PEG (600) on Nickel Rejection

The influence of PEG 600 in casting solution of CA\SSA at (100\0, 90\10, 80\20, 50\50 wt %) in solvent DMF on nickel concentration as25 mg\L illustrate that in figure (5) Rejection of the nickel ions follows a similar pattern for increasing concentrations of PEG in the membrane casting solution. However, there seems to be slight variation in the extent of rejection .In general, the PEG added membranes provide higher rejection for nickel ions .When the concentration of the blend membrane CA\SSA 100\0 wt%, the rejection of Ni (II) is 6-28% for PEG ranging from 0 to 10wt% while it is increase from 50%to 79% at CA\SSA 50\50 wt% for SSA increased from 0 to 50 wt%. This is because of the increased porosity while adding PEG, which is due to the higher hydrophilic nature of PEG. Indicate that cellulose acetate /sewage sludge ash blend membrane is comparatively superior in performance to a pure cellulose acetate membrane. Overall it was found that the membrane with composition 50% CA and 50% SSA and increase of PEG 600, the repulsive force between polymer segments along with leachability of PEG are enhanced and this favors the formation of macrovoides due to increase of number of large size pores [24]. Resulted produced permeate of desirable quantities when compared to similar membranes of other weight fractions under identical conditions.

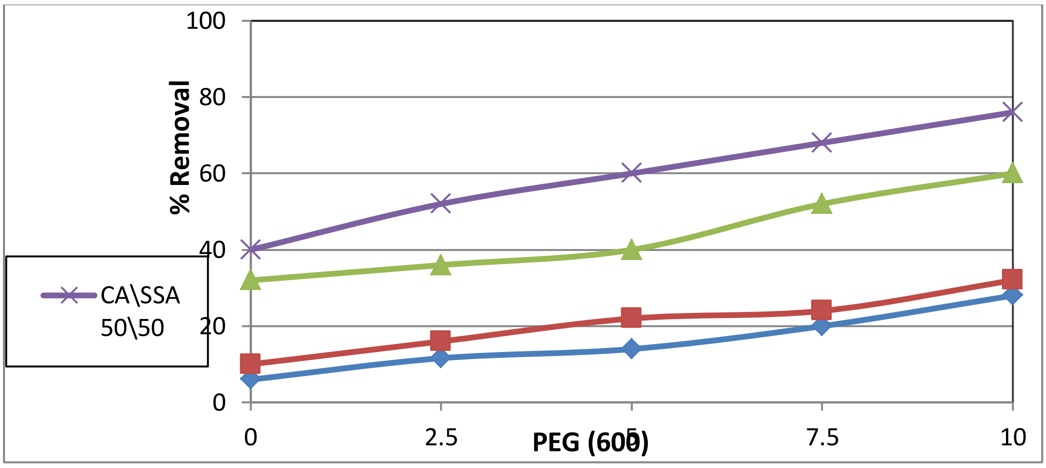

Figure (5) Effect of PEG (600) wt% on nickel removal using CA\SSA blend membrane

3.6 Effect of initial nickel concentration on the %removal of nickel using CA/SSA blend membrane

The effect of initial concentration on the percentage removal was investigated by varying the initial concentration of nickel between 5-20 mg\L at CA\SSA at 50\50 wt% was shown in figure (6) as can be seen, the removal efficiency 90% will remain high level at lower concentration 5mg\l and then decrease as the initial concentration is further increased at 20mg\l, the %removal resulted at 70%, it may be observed that CA\SSA blend membrane was ability for removal of nickel ions due to the in homogeneity arising as a result of the higher SSA content creating voids in the blend membranes .similar results were reported for cellulose acetate \sulfonated poly ether imide blend membranes by [25]

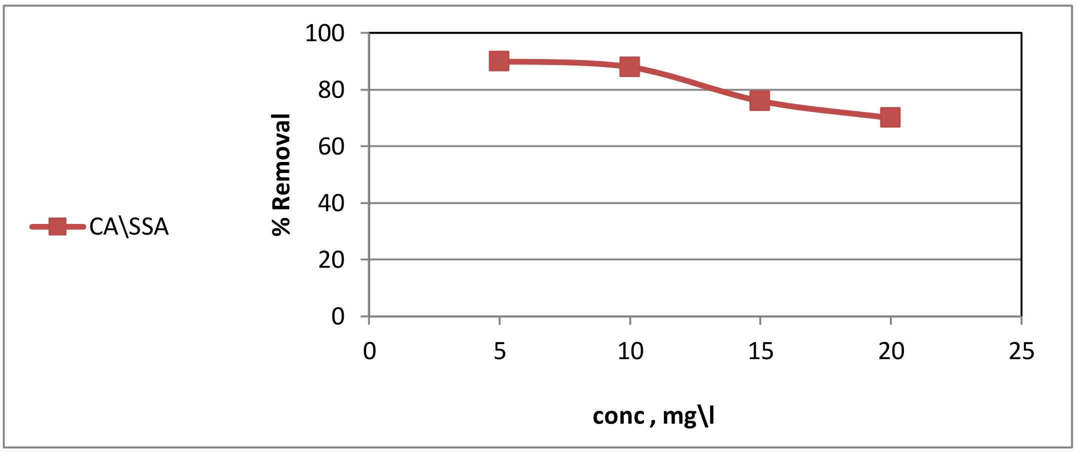

Figure (6) Effect of nickel concentration on %removal of nickel ions using CA\SSA at 50\50 wt%

3.7 Effect of hydraulic retention time of the blend membrane CA\SSA for %removal of Nickel ions

The effect of the hydraulic retention time of nickel ions at 25 mg\l on the blend membrane using CA\SSA at 50/50 wt% in presence of additives PEG600 at 10 wt% from 5 to 25 min, for determine the time required for % removal of Nickel ions ,which indicate in figure (7). The removal efficiency was recorded as 74,78,80,85 and 83% for 5, 10,15,20,25 min for time of the blend membrane CA\SSA respectively, the maximum efficiency at 20 min which reached 85% indicate the retention time increase % removal increase , this mechanism may include solute transfer to membrane which occurs diffusion through the pores to the internal adsorption sites .In initial stages of adsorption of nickel ions ,the concentration gradient between the film and the available pore sites is large and hence the rate of adsorption is increase , The rate of adsorption decreases in the later stages of the adsorption probably due to the slow pore diffusion of the solute ion into the bulk of the membrane.

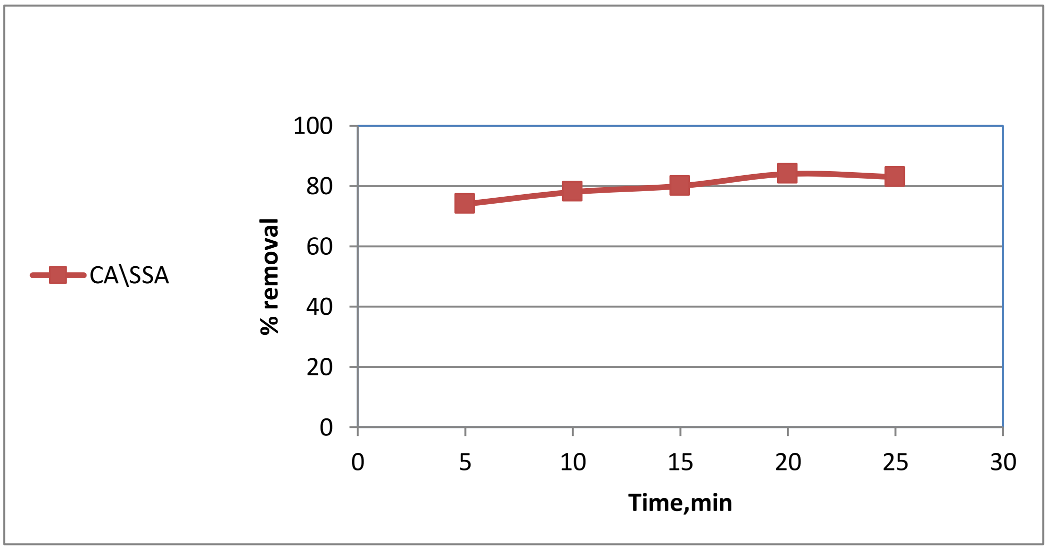

Figure (7) Effect of hydraulic retention time on% removal of nickel ions

3.8 Performance Evaluation of the CA\SSA Membrane on Abo-Rwash Waste Water Treatment Plant Effluent

The effluents of the plant were passed through CA\SSA blend membranes in the system used in figure (1) the membrane developed with 50/50 wt% from CA\SSA at 10 wt% from PEG, showed overall better performance compared to the other membranes. Particularly, table (1) analysis of wastewater treatment plant from Abo-Rawash before and after membrane pass through UF cell, which indicate CA\SSA was effectively removed the particles in colloidal size along with color removed as shown in figure (8), the reduction in TDS from 492 to 319 mg/L, Ammonia reduced from 13.42 to 7.2 mg/L, and COD from concentration 167 to 20mg/L. The results indicate that cellulose acetate /sewage sludge ash blend membrane was effectively active agent to remove and reduce the pollutant from wastewater.

Table (1) Chemical analysis of Abo-Rawash wastewater treatment plant before and after treatment with CA\SSA

Parameter	Effluent before treated	Effluent after treated	Removal%
pH	6.9	7.0	-
DO(mg/l)	1.8	2.3	-
Temperature(^{o}C)	28.5	25	-
Turbidity(NTU)	32.0	10.5	67
Colour	Gray	colorless	-
COD(mg/l)	167	20	88
BOD(mg/l)	96	11	88.5
Ammonia(mg/l)	13.42	7.2	46
Nitrate(mg/l)	0.69	0.35	49
TS(mg/l)	606	422	30.3
TDS(mg/l)	492	319	35
TSS(mg/l)	113	12	89

Figure (8) Images of wastewater from Abo-Rwash plant before and after treatment with CA\SSA blend membrane at 50/50 Wt%

4. Conclusions

The present study summarized the preparation of adsorptive membrane from cellulose acetate with blended sewage sludge ash (CA\SSA) in different compositions (100\0, 90\10, 80\20 and 50\50 wt%) and effect of organic additives PEG 600, where the water content increase from 78% to 86% at 100\0, 50\50 wt% of CA\SSA respectively when decreased of cellulose acetate from 100 to 50 wt% and increased of PEG from 0 to 10% wt, will be increased the pore size and porosity of membranes, increase SSA from 10 to 50 wt% improved the mechanical strength of blending membranes rather than used pure CA, finally determined the % rejection of nickel ions at 25mg\l from wastewater recorded 78% to 86% , finally applied the membrane on waste water treatment plant from abo-Rawash. Results indicated the CA\SSA at 50\50 wt% blend membrane has ability for removal of pollutants such as 88 ,88.5 and 89% of COD , BOD , and TSS respectively ,finally this research proved adsorptive membranes from CA\SSA at 50\50 wt% have many advantages, including high efficiency, good selectivity, low energy requirement and, possibly, large permeate flux.

5. References

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