The potential of nitrate removal from groundwater of Bani-Suif west area, Egypt using nanocomposite reverse osmosis membranes

Mohamed E. A. Ali and Abdel-Hameed M. El-Aassar*

Egyptian Desalination Research Center of Excellence & Hydrogeochemistry Dept., Desert Research Center, 1-Mathaf El-Mataryia St., Cairo, 11753, Egypt,
*Corresponding author; amelaassar@edrc.gov.eg & hameed_m50@yahoo.com,
Tel: +2 0100250154

Abstract

The excessive use of nitrogen-based fertilizers during flood irrigation, pesticide, waste disposal and industrial waste, seepage from septic tanks and evaporation processes during flood irrigation affects to the extent onto the groundwater quality of the shallow Quaternary aquifer of Bani-Suif west area, Egypt. A combination of major, heavy metals and nitrate has been used to characterize the groundwater in the investigated area. For this aspect, thirteen groundwater samples belong to that aquifer were collected. The total dissolved salts were varied between 327 and 2436 mg/l. Despite, the majority of the groundwater salinity was under the permissible limit for drinking, it was found to be unsuitable for human drinking, where they have had high concentrations of nitrate, which ranges from 366.41 to 1535.9 mg/l (exceeding the permissible limit, 45 mg/l). Because the aquifer has a high potentiality of groundwater, therefore, it is a must to re-use this high quantity of groundwater. Membrane technology was found to be the most suitable technique to overcome this problem. Therefore, three different types of thin film composite membranes (PA, PA/SiO$_2$, and PA/SW-CNT's) were prepared using the interfacial polymerization technique. The change of surface morphology of membranes because of addition of nanomaterials was characterized using Scanning Electron Microscopy, where the surface of the nanocomposite membranes was shown to be rougher than the unmodified membrane. In addition, the membranes were tested with a cross-flow apparatus to determine their performance in terms of water flux, salt rejection, and nitrate removal. However, the nanomaterials have been added to enhance the membrane water flux and even the salt rejection. It was observed that; nitrate rejection was shown to be decreased in the order of PA/SW-CNT's > PA/SiO$_2$ > PA. Where, PA/SW-CNTs reduced the nitrate concentration of a natural groundwater sample from 366.41 to 21.98 mg/l, i.e. under the permissible limit.

1. Introduction:

The excessive use of fertilizers for agricultural purposes in Egypt, especially nitrogen-based fertilizers has been increased significantly in the last decades due to overpopulation and expansion of agricultural zones, which results in contamination of the groundwater resources with nitrate compounds[1]. Consequently, the groundwater will be unsuitable for drinking because of the high solubility and stability of nitrate and its effect onto the human, especially the infants due to reduction of nitrate into nitrite, which reacts with hemoglobin forming blue baby Syndrome [2]. Different traditional and advanced techniques have been used for nitrate removals, among them bio-denitrification, ion-exchange, electrodialysis, electro-bioremediation, chemical reduction, distillation and Reverse Osmosis (RO) [3-6]. RO considers the common treatment processes that have been applied full-scale for nitrate removal from groundwater [2, 7]. The disadvantages regard to RO use, is the sensitivity to

scaling and fouling particularly if the feed water contains carbonate and sulfate ions of divalent cations [8]. Therefore, the addition of nanomaterials into the polyamide selective layer could develop the performance of the membranes in terms of water flux and salt retention. The nanomaterials that have been used for nitrate removal are nanoparticles, nanotubes, nanoclusters, nanoshells, nanofibers, and nanocomposites[9]. In addition, nanomaterials such as silica can improve the mechanical strength and thermal stability of membranes [10, 11]. Many previous works concluded that CNTs are significant and widely used as an adsorbent, as it has exhibited great potentials as an attractive adsorbent in wastewater treatment [12-14].

This article deals with the evaluation of the high concentrations of nitrate in the groundwater of west Bani Suif area and the possibility to treat it, even in fresh and/or brackish groundwater. This was achieved using prepared

nanocomposite RO membranes. In this study, the polyamide active layer of TFC membranes was prepared and modified using silica nanoparticles and/or single-wall carbon nanotubes to investigate the effect of surface area and high reactivity of these nanomaterials against nitrate retention or adsorption. Where nitrate molecules could be attached through physic-sorption or chemisorption on the surface of the nanomaterials. The effect of solution ionic strength on nitrate removal efficiency was investigated during RO experiment.

2. Study area description

Bani Suif governorate considers one of the Egyptian's ambitious national plans, especially because it belongs to the Nile valley. The area under investigation lies between 30º 46´ 36.1´´ and 30º 48´ 42.8´´ E and 28º 52´ 23.6´´ and 28º 54´ 16.8´´N, Fig.1. It occupies an area of approximately 10950 km^2 [15]. Fig. 2 shows the location and hydrogeological maps of the investigated area, where the main groundwater aquifer, which from water samples was collected is the Quaternary [16]. It is mostly fresh due to it is recharged by excess irrigation water and seepage from main and secondary canals [17].
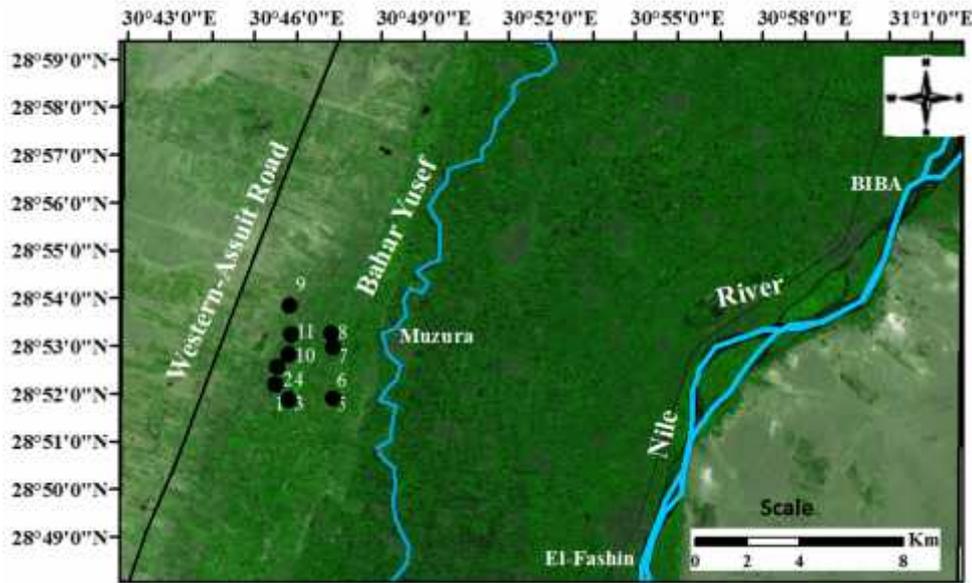

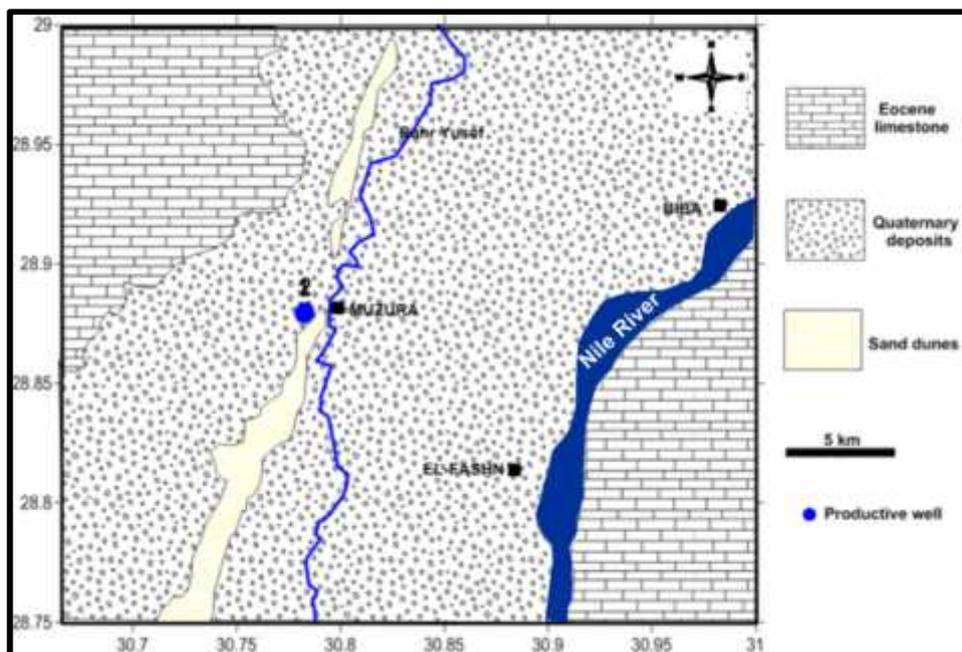Fig (1): GIS Location and wells location map of the study area

Fig (2): hydrogeological map of the study area

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3. Experimental:
3.1. Materials:

Polysulfone beds (Ps, Udel, P 3500 LCD MP7, M.W= 77000, Mn=22000); N, N-Dimethyl acetamide (DMAc), Fischer, 1, 3, 5-Benzenetricarbonyl tri-chloride, TMC (>98%), Sigma-Aldrich, m-phenylenediamine, MPD (> 99%), Across; n-Hexane, Merck were used as received without purification for preparation of TFC membranes. Commercial sodium nitrate and sodium chloride were used for the preparation of RO feed solution and different concentrations of nitrate.

3.2. Methods:

Collection and chemical analyses of groundwater samples: a field trip was carried out during 2016, Fig. 3 and thirteen groundwater samples were collected and analyzed according to standard methods adopted by Rainwater and Thatcher [18]. Electrical Conductance (EC) was measured using EC meter Model LF 538, WTW, USA and expressed in micromhos per centimetre (µS/cm). pH was determined using pH meter, 3320 pH meter (Jenway, UK). The major ions in the groundwater samples were determined using Ion Chromatography [19] (Thermo Scientific Dionex™ ICS-1100 Ion Chromatography System (Dionex ICS-1100). The heavy metals were analyzed using Inductive Coupled Plasma ((ICAP, 6500 Duo, Thermo Scientific, England).

The total NO_3 content was determined by Kjeldahl steam distillation [22]. The following equation was applied;

N, ppm (NO_3) = [(V-B)* normality of H_2SO_4*14*1000]/ ml sample

Where V and B are the volumes of titrant solution of the sample and the blank.

Ionic Balance (IB) is the percentage difference between the cations and anions sum present in water. It is calculated by the following equation;

$$IB = [(TC - TA)/ (TC + TA)] \times 100$$

Where, TC = Total cation, TA = Total anion in meq/l. The acceptable range for IB to clarify the water quality assessment is within ± 5.

Fig (3): Photographs of the field trip for groundwater samples collection during winter 2016

3.2.1. Preparation and Characterization of the membranes:

PA, PA/SiO_2, and PA/SW-CNT's membranes were prepared according to interfacial polymerization technique elsewhere [20, 21]. In brief, 16 % Ps solution was prepared as a sheet according to traditional phase inversion method, then an aqueous solution of MPD was poured onto a Ps sheet for 2 min. To avoid any defect in the prepared PA-TFC membrane, residual droplets of MPD aqueous solution on the top surface of the PS

membrane were removed before immersing in TMC solution by using a rubber roller. Afterwards, TMC in organic solution was reacted for 1 minute with MPD saturated Ps membrane. In case of using SiO₂ and CNTs, TFC membranes were prepared as membrane control, except the nanomaterials were added to the hexane solution with sonication for at least 60 min until obtaining homogeneous solutions. The obtained membrane surface was washed with hexane and left to dry for 10 minutes at 85°C. Eventually, the obtained membranes were kept in Deionized water (DI) until characterization and application in desalination using cross-flow experiments.

The membrane surface morphology was characterized by using scanning electron microscope (SEM) (Quanta FEG 250 microscope) and the mechanical properties were estimated using Dynamic Mechanical Analysis, DMA TAQ800 (Film tension clamp).

3.2.2. Evaluation of the membranes Performance:

Processes of RO were carried out using laboratory reverse osmosis test unit, model LAB-20, manufactured by the Danish Sugar Corp., LTD>, Denmark, with an effective membrane area of 0.018 m², Fig. 4. All

membranes were pressurized with DI for 1 hour10 bar prior to the determination of nitrate ion separation properties. After that, different concentrations of sodium nitrate solution (100, 500, 1000 and 1500 mg/l & 73 to 1094 ppm as nitrate) prepared by dissolving sodium nitrate in DI water were pressurized against the prepared membranes. The effect of ionic strength was investigated through mixing two concentrations of sodium chloride (1000 and 2000 mg/l) with sodium nitrate solutions at different applied pressures in both cases. However, salt rejection (R_s %) and the water flux (J_v) of the membranes were calculated as follows:

$$R_a\% = \frac{(C_f - C_p)}{C_f} \times 100$$

Where C_f and C_p are the concentrations of the feed and permeate water (product), respectively.

$$J_v = \frac{Q}{A \times t}$$

Where Q is the collected permeate water (liter), "A" is the membrane surface area (m²) and "t" is the time (h).
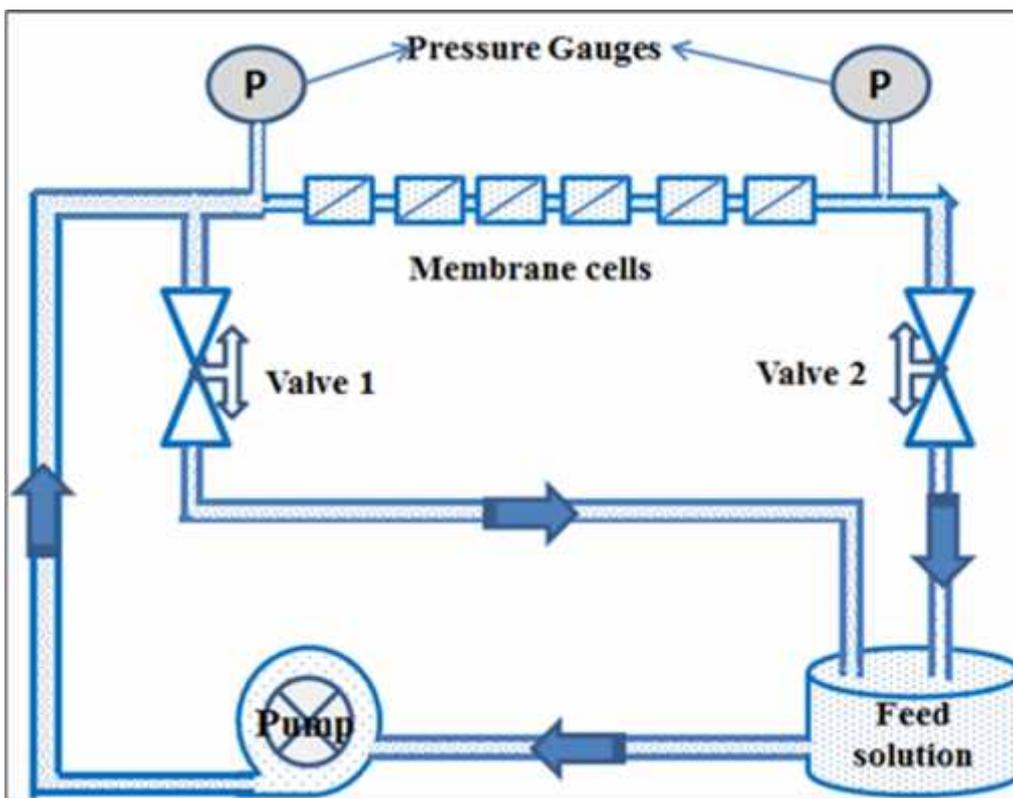
Fig (4): Schematic representation of the RO test unit

4. Results and Discussion:

4.1. Evaluation of groundwater quality for drinking

Thirteen groundwater samples were collected from the study area in 2016. The field measurements of them were shown in Table (1). It was found that the depth to water ranged between 5 and 9 m, which reveal that all

groundwater is shallow and can be affected extensively by seepage of the surface water. The physico-chemical analysis of the collected groundwater samples are shown in Table (2).

Table (1): The locations and the field measurements of the collected groundwater samples

Sample No.	Latitudes (N)	Longitudes (E)	EC (µS/cm)	Temperature (ºC)	Depth to water (m)
1	28º 52´ 48.1´´	30º 46 ' 55.9´´	1762	23.5	6.5
2	28º 52 ' 23.6´´	30º 46 ' 36.9´´	1485	25.9	9
3	28º 52 ' 35.1´´	30º 46 ' 50.9´´	1108	26.4	9
4	28º 52 ' 32.1´´	30º 46 ' 54.7´´	1667	25.6	9
5	28º 52 ' 37.5´´	30º 47 ' 39.1´´	2257	25.1	9
6	28º 52 ' 38.4´´	30º 47 ' 07.1´´	2188	25.5	6
7	28º 53 ' 19.1´´	30º 47 ' 10.0´´	1494	25.4	5
8	28º 53 ' 46.4´´	30º 47 ' 07.6´´	3708	26.4	6.5
9	28º 54 ' 16.8´´	30º 46 ' 36.1´´	4025	25.6	8
10	28º 53 ' 12.8"	30º 46 ' 34.5"	1276	25.1	6
11	28º 53 ' 15.0´´	30º 46 ' 53.9´´	2255	25	7
12	28º 52 ' 38.4´´	30º 46 ' 49.5´´	712	25.6	9
13	28º 52 ' 42.2´´	30º 46 ' 54.0´´	1459	24.3	8

Table 2: Physico-chemical characteristics of the collected groundwater samples

No.	pH	Ec (um/cm)	TDS (mg/l)	Unit	Ca^{++}	Mg^{++}	Na$^+$	K$^+$	Total cations	CO$_3^-$	HCO$_3^-$	SO$_4^-$	Cl$^-$	NO$_3$	Total anions
1	7.3	1762	1128	mg/l	180.0	62.00	55	14	16.829	15	204.35	365	46.28	288.8	17.403
				me/l	8.982	5.099	2.391	0.357		0.5	3.349	7.592	1.305	4.66	
2	7.4	1485	950	mg/l	160.5	42.56	54	6	14.012	15	204.35	192	44.99	333.2	14.485
				me/l	8.011	3.500	2.348	0.153		0.5	3.349	3.994	1.269	5.37	
3	7.6	1108	710	mg/l	124.00	28.00	46	7	10.669	24	183.00	61.2	34.71	293.1	10.777
				me/l	6.188	2.303	2.000	0.179		0.799	2.999	1.273	0.979	4.73	
4	7.2	1667	1067	mg/l	200.0	55.00	35	9	16.255	15	201.30	320	41.13	291.7	16.319
				me/l	9.980	4.523	1.522	0.230		0.5	3.299	6.656	1.160	4.70	
5	7.4	2257	1445	mg/l	180.0	135.00	63	23	23.410	18	207.40	480	251.95	190.1	24.154
				me/l	8.982	11.102	2.739	0.587		0.599	3.399	9.984	7.105	3.07	
6	7.6	2188	1401	mg/l	205.0	66.00	120	11	21.155	21	158.60	385	215.96	297.4	22.193
				me/l	10.230	5.428	5.218	0.281		0.699	2.599	8.008	6.090	4.80	
7	7.5	1494	956	mg/l	145	52	65	7	14.517	24	213.50	190	70.70	296	15.018
				me/l	7.236	4.276	2.826	0.179		0.799	3.499	3.952	1.994	4.77	
8	7.3	3708	2373	mg/l	246	102	380	16	37.594	18	158.60	570	704.43	257.4	39.071
				me/l	12.275	8.388	16.522	0.408		0.599	2.599	11.856	19.865	4.15	
9	7.2	4025	2576	mg/l	280	108.10	400	27	40.943	15	183.00	640	732.71	281.7	42.017
				me/l	13.972	8.890	17.392	0.689		0.5	2.999	13.312	20.663	4.54	
10	7.4	1276	817	mg/l	120.00	35.000	75	8	12.331	0	244.00	143.75	73.27	240.2	12.929
				me/l	5.988	2.878	3.261	0.204		0	3.999	2.990	2.066	3.87	
11	7.2	2255	1443	mg/l	210	46.5	160	9	21.489	0	228.75	340	215.96	347.5	22.516
				me/l	10.479	3.824	6.957	0.230		0	3.749	7.072	6.090	5.60	
12	7.5	712	456	mg/l	84.71	18.48	36	5	7.440	15	204.35	80.6	30.85	82.9	7.732
				me/l	4.227	1.520	1.565	0.128		0.5	3.349	1.676	0.870	1.34	
13	7.4	1459	934	mg/l	145	38	80	7	14.018	0	228.75	210	44.99	294.6	14.137
				me/l	7.236	3.125	3.478	0.179		0	3.749	4.368	1.269	4.75	

It was observed that about 46 % and 54 % of groundwater samples are fresh (less than 1000 mg/l) and brackish, respectively. However, high salinity may be due to the presence of shale beds within the water-bearing formations that causes a little recharge to such wells and/or due to the over-pumping from these wells.

The suitability of groundwater for the drinking purposes was performed by comparing the ions concentration with that of the World Health Organization (WHO, 2011) and Egyptian standards (2007). First of all, it was observed that the majority of the groundwater samples were biologically and chemically safe except the high nitrate concentrations. Table 2 reveals that the majority of groundwater samples in the studied area are suitable for drinking in salinity aspect, where their TDS were below the standard permissible limit (1000 mg/l). In addition, all heavy metal concentrations were under the permissible limit, where no concentrations were detected by ICAP. It

was observed that, the only problem restricting the use of this groundwater is the high concentration of nitrate (Table 2), which had shown to be ranged from 82.9 to 347.50 mg/l (exceeding the permissible limit, 45 mg/l[2]). These high nitrate concentrations might be due to the excessive use of nitrogen-based fertilizers that seeped into the shallow groundwater, where the depth to the groundwater about 9 m. at maximum. Fig. 5 shows a geo-electrical profile, East and west sample No. 1, which confirms that the formation and the thickness of the upper layer of the aquifer, which formed from coarse sandy soil can allows the seepage of irrigated water contaminated with nitrogen-based fertilizers into the shallow groundwater. Quantitative interpretation of the field curves revealed that the geoelectric succession in the study area consists of five groups of geoelectric layers named surface layer (geoelectric layer A and B), dry sand with clay interbeds, saturated sand and gravels with few clay intercalations

(geoelectric C), saturated fine sand with clay interbeds (geoelectric D) and finally clay layer (geoelectric E). The geoelectric layer D represents the main water bearing unit and its thickness ranges between 26 m and 30 m, while its groundwater salinity reaches about 1000 ppm.
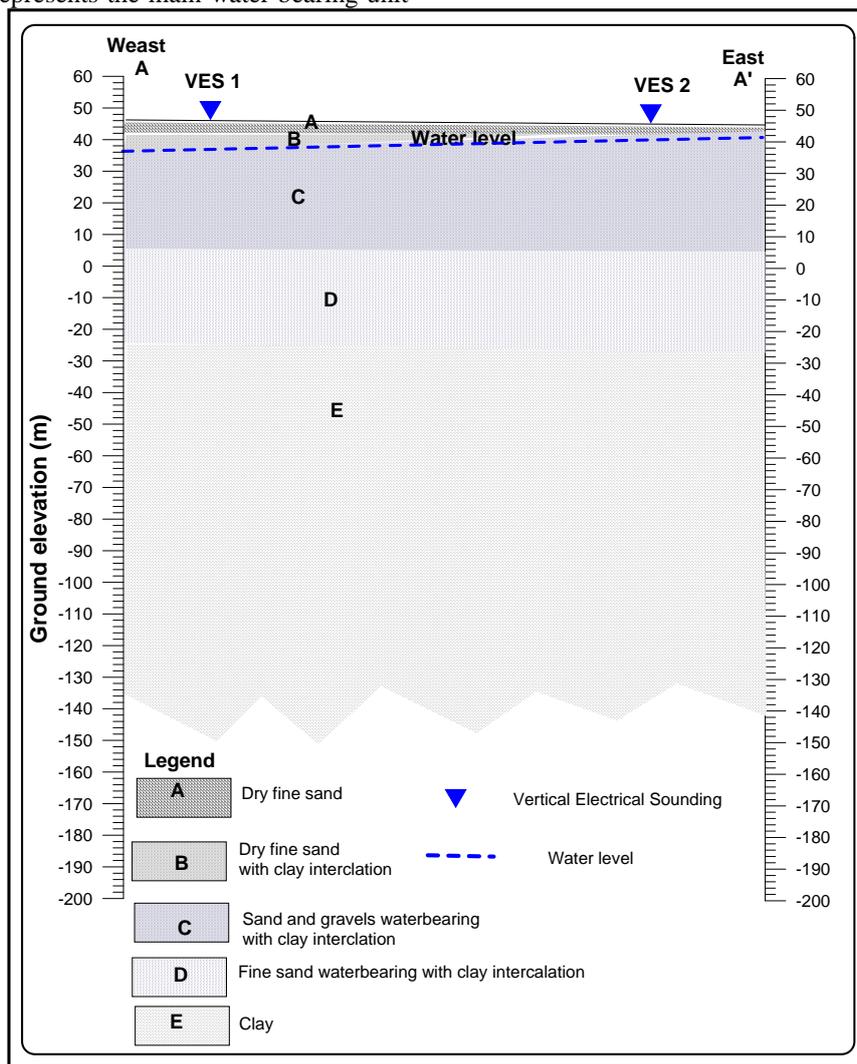

Fig (5) Geo-electrical profile of the quaternary aquifer in the investigated area

4.2. Water flux and salt rejection

The membrane permeation test and separation ability were tested using the feed solution of 2000 mg/l NaCl, which was dissolved in DI water. Table (3) illustrates that the salt rejection of the polyamide membranes in-significantly changed with additional SiO_2 and SW-CNT's. Whereas, the water flux was abruptly increased from 29.3 L/m^2.h for PA to 35.64 and 47.52 L/m^2.h for PA/SiO₂ and PA/SW-CNTs, respectively. The increasing of water flux with addition of silica is due to its hydrophilic surface properties which could attract more water molecules onto the membrane surface [22]. In case of membranes modified with CNT's, the directed water channels were formed through the formation of an interface between the cross-linked CNT's and the polymer matrix, which enhance the passage of water within the porous CNT's[23]. Moreover, CNT's provide a uniform pore distribution, a large specific surface area in addition to their various surface functional groups. Therefore, the

high surface area and high reactivity of the nanomaterials enable them to be used as adsorbents, where, nitrate molecule could be attached through physic-sorption or chemisorption on the surface of the nanomaterials. This high affinity to adsorption of nitrate molecules onto PA/SiO₂ and PA/SW-CNT is owing to the innate surface area and external functionalization in case of silica[24].

Table 3 water flux and salt rejection of the prepared membranes

Parameter	PA	PA/SiO₂	PA/SW-CNT
Water flux (L/m^2.h)	19.3	35.64	47.52
Salt rejection (%)	95	97.69	97.1

Fig. 6 shows SEM of the three prepared membranes to illustrate effect of SiO_2 nanoparticles and CNT's incorporation in the membranes matrix onto its surface morphology. It was noticed that SiO_2 nanoparticles and CNT's showed much effect on the overall morphology of TFC membrane, which changes from smooth to rough. In

other words; the surface roughness of the PA/SW-CNTS nanocomposite membrane is greatly increased relative to control PA membrane. While in case of PA/SiO$_2$, the addition of silica nanoparticles can be observed as spherical particles within the membrane structure with a change of the surface morphology [25]. Moreover; the surface of nanocomposite membranes has ascendant and broadened ridge–valley structure compared to PA membrane, which confirms variation on surface roughness [26]. However, the rough surfaces can absorb water molecules more than smoother one which confirm the high water flux of the nanocomposite membranes.

4.3. Removal of nitrate salts using membranes

Fig. 7a illustrates the behaviour of the PA, PA/SiO$_2$ and PA/SW-CNTs membranes in the removal of nitrate at different applied pressure. It was observed that, as applied pressure increases from 5 to 15 bars, the nitrate rejection was shown to be decreased for PA and PA/SiO$_2$ whilst it increased in the case of PA/SW-CNTs. The adverse effect of the applied pressure on the performance of PA and PA/SiO$_2$ might be due to enlarging the pore size of these membranes because their low mechanical strength.
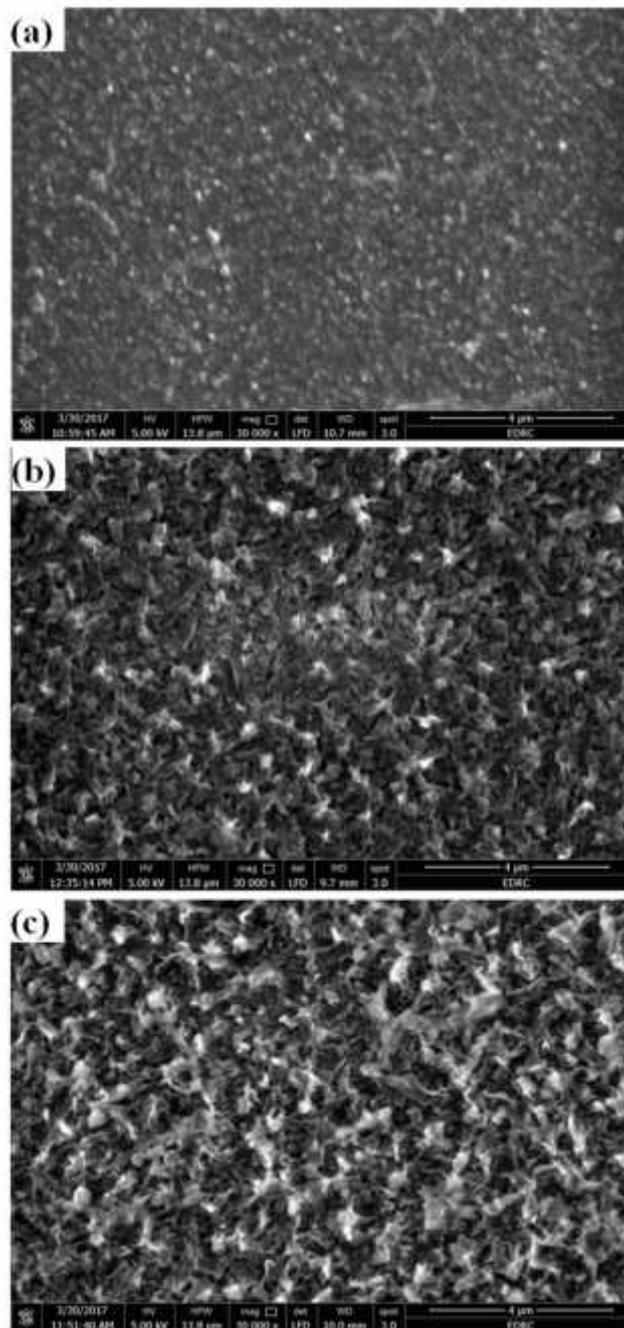

Fig (6) SEM images of (a) neat, (b) SiO$_2$ and (c) CNT$_s$ modified TFC membranes
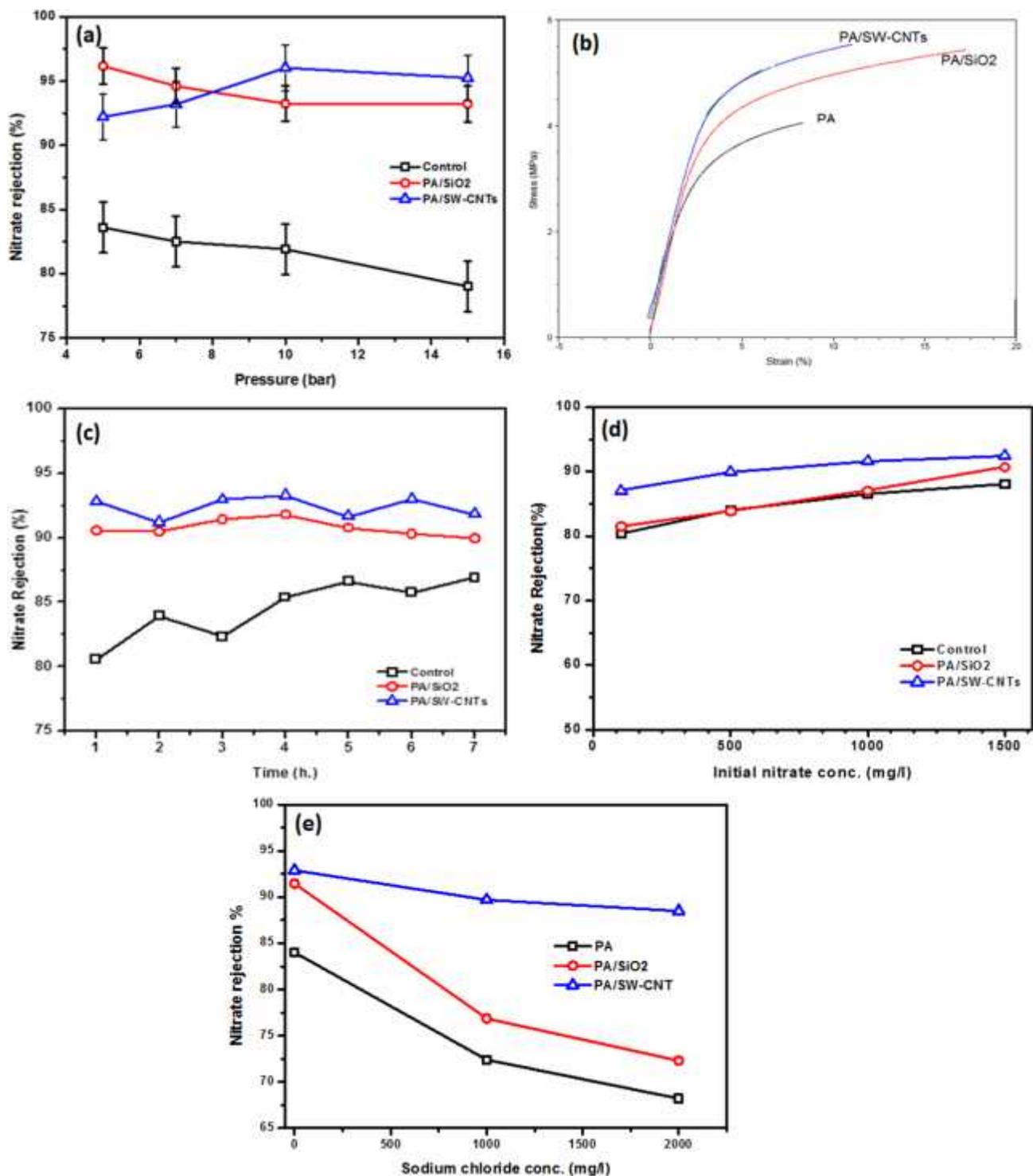
Fig (7): Membranes characteristics and performance; a) effect of hydraulic pressure onto nitrate rejection, b) mechanical stability of different membranes, c) nitrate rejection as a function of time, d and e) effect of initial concentration and sodium chloride concentration onto nitrate rejection

Membrane stability against pressure as a function of the addition of CNT's was observed due to the sufficient mechanical stability of the CNT's composite membrane. As illustrated in Fig. 7b, the mechanical strength of the membranes decreases in the order of PA/SW-CNTs >

PA/SiO$_2$ > PA. Moreover, membrane stability was investigated through evaluating the performance at 10 bars for about seven hours, Fig. 7c. It was found that all membranes show no significant decline in the water flux with a constant rejection of nitrate ions. However, the high

nitrate rejection in case of control membrane may be due to blocking of membrane pores and cake formation that lead to more rejection of the nitrate ions[27, 28].

The effect of initial nitrate concentration in the range of 100-1500 mg/l on the removal efficiency using the three prepared membranes is illustrated in Fig. 7d. For all of the investigated membranes, it was observed that the nitrate retention increased as a function of initial concentration increases. This is against the normal phenomena. This can be explained on the basis of more ions in solution lead to blocking the pores of the membranes and provide a negative charge on the membrane surface. Hence, nitrate ions in the feed solution would repel with the membrane negative charges and increase the ions rejection. In general, the ion rejection using reverse osmosis decreases as initial concentration increased. In the investigated figure, the salt rejection insignificantly changed because of change of the applied pressure. Where nitrate retention rises with an increase in the hydraulic pressure.

Actually, the natural surface or groundwater contains different salt and the more dominant one is sodium chloride. In addition, the performance of RO rejection depends on the characteristics of solute and membrane type. Therefore, the effect of ionic strength on the nitrate removal of the membranes was investigated using mixing sodium chloride at two concentrations of 1000 and 2000 mg/l with sodium nitrate; at the same applied pressure of 10 bar and nitrate initial concentration of 100 mg/l, Fig.7e. From the figure, there was a general decreasing trend of the three membranes for the removal of nitrate as NaCl concentration increases from 1000 to 2000 mg/l. One can see that the decline of rejection in case of PA/SW-CNTs is less than that of PA and PA/SiO$_2$, which might be due to the difference in the membrane characteristics because of mechanical stability and uniform pore structure of PA/SW-CNTS's membrane. However, the influence of the ionic strength of the feed solution on the nitrate removal could be explained as follows; 1) sodium and chloride ions that are smaller in the ionic radius (0.95 and 1.81 Å, respectively) compared to nitrate ions, 1.96 Å [29] would

compete with nitrate ions for a limited number of pores and charges on the membrane surface. 2) The ionic strength would affect the activity coefficient nitrate ions and thus enhance its transfer through the membranes [12]. On the basis of the above results, it can be concluded that sodium chloride has a strong effect on nitrate rejection using the membranes. In this figure, we studied the effect of solution strength on nitrate rejection. More specifically, the influences of chloride ions on the rejection of the sodium nitrate salt. Where, the concentration of nitrate ions was maintained constant, whereas that of the chloride anion was changed. It was observed that as the concentration of sodium chloride increases, nitrate retention was generally decreased, which has been similarly observed and explained in the literature [30, 31]. This can be explained on the basis of the similarity in characteristics of nitrate and chloride ions, where there is no preferential transport of one of the anions with regard to the other in the presence of sodium ion. However, the increase in sodium ion concentration resulted in enhanced charge shielding and hence reduced retention based on charge repulsion [32, 33]. Moreover, the addition of sodium chloride strongly neutralizing the membrane charge by positive sodium ions, therefore it could decline of the membrane anions repulsion.

Table 4 shows concentrations of major ions and nitrate before and after desalination of a fresh groundwater sample (well No. 12) using PA/SW-CNTs membrane. Where the nitrate concentration was decreased from 82.9 mg/l to 8.29 mg/l, which is under the permissible limit according to WHO and Egyptian standards. As we mentioned before, the concentration of nitrate in the groundwater samples ranged between 82.9 to 347.5 mg/l mg/l, therefore, its concentration after 90 % rejection, will be 35 mg/l, i.e. under the permissible limit (45 mg/l). Moreover; this rejection at these high concentrations may be good, where many previous studies [34-36] used a low concentration of nitrate with a less efficient compared to our work.

Table 4: Chemical characteristics of a groundwater sample before and after desalination using PA/SW-CNTs membrane

Parameter	Before	After	Egyptian Standards (2007)	WHO (2011)
TDS	456	38.8	1000	1000
pH	7.5	7.2	--	6.5-9.2
Sodium	36	1.68	200	200.00
Potassium	5	2	--	--
Calcium	84.71	6.2	150	--
Magnesium	18.48	9.1	50	--
Chloride	30.85	4.2	250	250
Sulfate	80.6	8.4	250	400
Carbonate	15	0	--	0.5-1
Bicarbonate	204.35	13.5	--	4
Nitrate	82.9	8.29	45	45

Conclusions

The chemical analysis of some collected groundwater samples from the Quaternary aquifer, in the reclaimed areas of West Bani-Suif governorate, Upper Egypt reveals the effect of excessive use of fertilizers on water quality. The water salinity of the samples was ranged between 456 to 2576 mg/l, i.e. from fresh to slightly brackish. 46% from total samples were under the permissible limit (1000 mg/l) but it is not suitable for human drinking because of the high concentration of nitrate, which ranged from 82.9 to 347.5 mg/l (exceeding the permissible limit, 45 mg/l). Therefore, thin film nanocomposite membranes were prepared and used for nitrate removal using. The concentrations of nitrate before and after desalination of a fresh groundwater sample using PA/SW-CNTs membrane showed that its concentration decreased from 82.91 mg/l to 8.29 mg/l that is under the permissible limit according to WHO and Egyptian standards.

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