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Removal of nitrate, phosphate and COD from synthetic municipal wastewater treatment plant using membrane filtration as a post-treatment of adsorption column

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ABSTRACT

A pilot study was designed so as to study the methods of reusing wastewater from effluent of municipal wastewater treatment plant and recycling wastewater into sanitary water. The pilot design was based on two stages: adsorption column and membrane method. The highest removal efficiency was achieved in RO membrane as a post treatment of activated carbon. The optimum pressure of each membrane and its combination with adsorption column was achieved by applying four different pressures, the aim of which was to find out the removal efficiency of system at different pressures, considering the appropriate permeate flow rate. In this situation, removal efficiencies of nitrate, phosphate and COD at optimum pressure were 98.9, 99.3 and 95.2%, respectively. It is remarkable that NF membrane was also shown to be performing properly in terms of removal efficiency. Removal efficiencies for nitrate, phosphate and COD in NF membrane as a post treatment of activated carbon were 95.4, 98.8 and 90.4%, respectively. The permeate flow rate of NF membrane is approximately 50% greater than that of RO. Additionally, activated carbon performed more strikingly in terms of removal efficiency, than the mixture of activated carbon-sand as a pre-treatment method, as the porosity of aggregate decreases the removal efficiency of all parameters decreases consequently. Furthermore, the adsorption column is not well-suited to TDS and EC removal.

Keywords: Treatment; Municipal wastewater effluent; Reverse osmosis; Nano filtration; Adsorption column

1. Introduction

As the population of the world is growing at a rapid pace, more water is required. Population growth may result in a higher amount of produced wastewater as well. Since water resources are severely restricted, most of which are not even accessible or cost-effective to be treated, reusing wastewater and sewage flows has become crucial. In stark contrast to previous approach to wastewater treatment, which induced only to the removal of organic matters or microbial pollutants, these days, removal of other pollutants such as nitrate, phosphate and so forth has become very crucial [1]. The commonly-used treatment methods for nitrate removal include chemical denitrification using zero-valent iron, zero-valent magnesium, ionic exchange, reverse osmosis, electro-dialysis, catalytic denitrification and biological denitrification [2–10]. Generally, reverse osmosis, ion exchange and electro-dialysis processes are considered as the best available technologies to treat nitrate-contaminated water [11–13]. Comparatively, adsorption seems to be a more attractive and viable method for the removal of nitrate in terms of cost, simplicity of design and operation [14–22].

In 1995, Cevaal et al. used reverse osmosis method (RO) to remove nitrate from wells of Brighton. Pilot studies proved that RO membranes would remove nitrate up

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to 97% [23]. In 2002, Schoeman et al. studied the removal of nitrate using RO membrane method in a rural area in Northern Africa, where they managed to reduce nitrate from 42.5 mg/l to 0.9 mg/l (97.9%). They also reported that TDS decreased from 1292 mg/l to 24 mg/l (98.1%) [7]. Van der Bruggen and Vandecasteele conducted a research to remove pollutants from surface and groundwater flows using NF membrane. They reported that NF was a suitable approach to remove wide range of pollutants from surface and groundwater. It could be usually used to remove natural organic materials, microbial pollutants, viruses, bacteria, nitrate, arsenic and execute desalination [24]. Kim et al. tried to treat wastewater of stainless steel factory containing high amount of nitrate using RO and NF methods. The results showed that RO membrane could remove more nitrate than NF membrane did. Removal efficiency declined as pH decreased; conversely as nitrate concentration increased [25]. In 2010, Richards et al. considered the influence of pH on the removal of fluorine, boron and nitrate in RO and NF methods. Results showed that removal of fluorine and boron depended on the type of membrane and pH, while removal of nitrate depended on the type of membrane rather than pH [26]. Naushad et al. tested fate of De-Acidite FF-IP anion exchange resin for adsorptive removal of removal from synthetic and commercially available bottled water samples. The breakthrough capacities in Milli-Q and tap water were 35 and 30 mg/g, respectively, optimum recovery (93%) was observed with 0.1 M NaOH and optimum adsorption was observed at pH range 2–6 [27]. In 2016, Khan et al. developed the UPLC-ESI/MS method to quantify $NO3^-$, $BrO3^-$ and $NO2^-$ in metropolitan water and commercial bottled water after mere filtration steps. The quantified levels of $NO3^-$ were not found to pose a risk [28]. In 2016, Kamaraj et al. studied the removal of nitrate from water by electrocoagulation process using zinc and stainless steel as anode and cathode respectively. They came up with the fact that a current density of 0.10 A , pH of 7.0 and an inter electrode distance of 0.005 m were considered as optimum conditions for the removal of nitrate with maximum removal efficiency of 69% [29]. Removal of phosphate was investigated using electrocoagulation, microfiltration, membrane bioreactors, NF and RO [30–35]. Hong et al. compared commercial NF90 membranes (rejection of phosphate more than 97%) with poly styrene sulfonate (PSS)/poly diallyldi methyl ammonium chloride(PDADMAC) films deposited on a porous alumina support (rejection 98%) but with lower solution flux for NF90 membrane [35]. In 2011, Dolar et al. considered the removal of fluoride and phosphate from Fertilizer Company using RO and NF membranes. The results indicated that removal of phosphate was over 97% in NF membrane for real wastewater and more than 96% in RO for real wastewater [36]. Naushad et al. prepared pectin based quaternary amino anion exchanger (Pc-QAE) using simple crosslinking polymerization method. The adsorption process, which was pH dependent, showed maximum adsorption of phosphate anions at pH of 7. The adsorption of phosphate anions onto Pc-QAE followed pseudo-second order kinetics and the equilibrium data fitting well with the Langmuir isotherm model indicated the monolayer adsorption. Thermodynamic results showed that phosphate anion adsorption was endothermic and spontaneous in nature [38].

Adsorption technology has been successful in removing various types of inorganic anions; such as fluoride, nitrate, bromate and perchlorate, using various materials as adsorbents [39–50]. In 2012, Al-Othman et al. used activated carbon prepared from peanut shell by chemical activation with KOH, and was afterwards characterized and utilized for the removal of Cr(VI) from aqueous solutions in the concentration range of 10–100 mg/L. Effective adsorption was witnessed in the pH range of 2–4. The percentage removal decreased with an increase in initial concentration [51]. In 2014, Alshehri et al. synthesized a novel bio-based polymeric adsorbent curcumin formaldehyde resin (CFR) via poly condensation of curcumin (a natural bis-phenol) and formaldehyde. The removal rate of phenol using CFR was very fast, and equilibrium was established within 60 min. Kinetic studies showed better applicability for pseudo-second-order model. The Freundlich isotherm exhibited the best synchronization with the experimental data [52]. In 2017, Alqadami et al. synthesized a novel magnetic metal−organic framework composite composed of iron oxide magnetic nanoparticles and AMCA-MIL-53(Al). The adsorption capacity was calculated to be 227.3 and 285.7 mg/g for U(VI) and Th(IV), respectively, by fitting the equilibrium data to the Langmuir model. The kinetic studies demonstrated that the equilibrium time was 90 min for each metal ion. The adsorbed metals were easily recovered by desorption in 0.01 M HCl [53]. In 2017, Mu. Naushad et al. prepared nickel ferrite bearing nitrogen-doped mesoporous carbon ($NiFe_2O_4$-NC) using polymer bimetal complexes and used with the aim of removing Hg^{2+} from aqueous medium. The adsorption isotherm could be well described with Langmuir model, with the maximum adsorption capacity of 476.2 at 25°C. The results designated that the adsorption followed the pseudo-second-order kinetic model smoothly. The desorption results were indicative of the best recovery of Hg^{2+} metal ion using 0.01 M HCl [54]. In 2016, Albadarin et al. produced activated lignin-chitosan extruded (ALiCE) pellets with controlled particle size distribution (almost spherical: dp~500_1000μm) for efficient methylene blue adsorption. The experimental data fitted well with the Langmuir isotherm (= 0.997), yielding a maximum adsorption capacity of 36.25 mg/g and the pseudo second-order model with intraparticle processes initially controlling the process of MB adsorption [55]. In 2017, Ghasemi et al. evaluated the performance of two new adsorbents, ash and Fe nanoparticles loaded ash (nFe-A) for the removal of Pb(II) from aqueous solution. Equilibrium data fitted very well with the Langmuir isotherm model. Kinetics studies showed better applicability for pseudo-second-order model for both adsorbents. The breakthrough capacities of ash and nFe-A for Pb(II) removal was found to be 25 and 30, respectively [56]. It is worth noting that the selection of suitable adsorbents for the removal of a particular type of anion is very important, which makes it possible to achieve optimal elimination efficiency. Activated carbon is the most commonly-used adsorbent in the removal of various pollutants.

In the present study a novel method, a combination of adsorption column and membrane, was used to acquire the best results. Also, the very reusing of effluent of wastewater treatment plant, recycling wastewater into sanitary water and saving water in a water crisis period are of cardinal importance in this research, as they have never been previously employed. Activated carbon and sand column were employed as a pretreatment of membrane. The RO and NF membrane were, in turn, compared separately to understand the removal efficiency of nitrate, phosphate and COD; combining RO and NF membrane with adsorption column was carried out to maintain the highest removal efficiency.

2. Materials and methods

2.1. Experimental site

The pilot was set up in a wastewater treatment plant in Tehran, Iran, all the pertaining experiments of which were performed there accordingly. The southern Tehran wastewater treatment plant, located in Shahr Rei adjacent to Emadavar village, is specified for the treatment of Tehran's sewage in 8 modules with a capacity of 4,200,000 people. The four existing modules cover a population of 525,000 people, and a flow of 450,000 m^3/d can be treated. The treated wastewater will provide irrigation of agricultural land in Varamin plain.

2.2. Wastewater characteristics

In this research, samples were collected from the effluent of conventional activated sludge system from wastewater treatment plant in Tehran, Iran. All parameters of the effluent were determined using standard methods for the examination of water and wastewater [37]. The analysis of effluent is shown in Table 1. All experiments were performed at constant temperature of 25°C and pH = 7.5.

After determining the characteristics of effluent, synthesis of effluent was made through compounds that had been purchased from Merck group in Germany. The synthesis used materials are shown in Table 2.

2.3. Experimental variables

a) Variables of membrane system included operating pressure and nitrate concentration.
b) Variables of adsorbent column are nitrate concentration, characteristics of media together with the porosity of aggregate.

2.4. Membranes characteristic

All characteristics of applied membranes in this study are presented in Table 3.

2.5. Experimental setup

Figs. 1 and 2 illustrate the schematic diagram of the experimental setup. Activated carbon cartridge was used to remove odor, taste and chlorine. Operating temperature of the cartridge is 4.4 to 51.6°C; and so was true of MF, used to remove sand, silt and turbidity. Also the operating temperature of the cartridge is 52°C.

Table 1
Characteristics of wastewater treatment plant effluent

Parameter	Initial value
pH	7.5
Temperature, °C	25
BOD, mg/l_5	15
COD, mg/l	20
TSS, mg/l	16
TDS, mg/l	430
NO_3–N, mg/l	90
PO_4–P, mg/l	7

Table 2
Synthesis compounds

Parameter	Synthesis compound
pH	HCL and NaOH
BOD_5	Sugar
COD	Starch
TSS	Bentonite
TDS	Salt
NO_3–N	Sodium nitrate
PO_4–P	Monosodium phosphate

Table 3
Characteristics of membranes

Membrane	NF	RO
Model	FilmTec N90-4040	FilmTec BW30-4040
Type	Polyamide thin film composite	Polyamide thin film composite
Active area (m^2)	37	41
Maximum operating pressure (bar)	12	41
Maximum operating temperature (°C)	40	45
pH range	3-11	2-11
Free chlorine tolerance (ppm)	0.1	0.1

2.6. Characteristics of adsorbents

In this study, granular activated carbon was used as an adsorbent in activated carbon column. The adsorbent was placed inside a cylinder with the following measurements: diameter = 25 cm, height = 65 cm. In the following step, activated carbon was mixed with standard sand that was used as an adsorbent in adsorption column. Specific gravity of activated carbon and sand is 600 kg/m^3 and 1500 kg/m^3, respectively. The characteristics of activated carbon are depicted in Table 4. Also, a comparison between sand and activated carbon gradation is shown in Table 5.

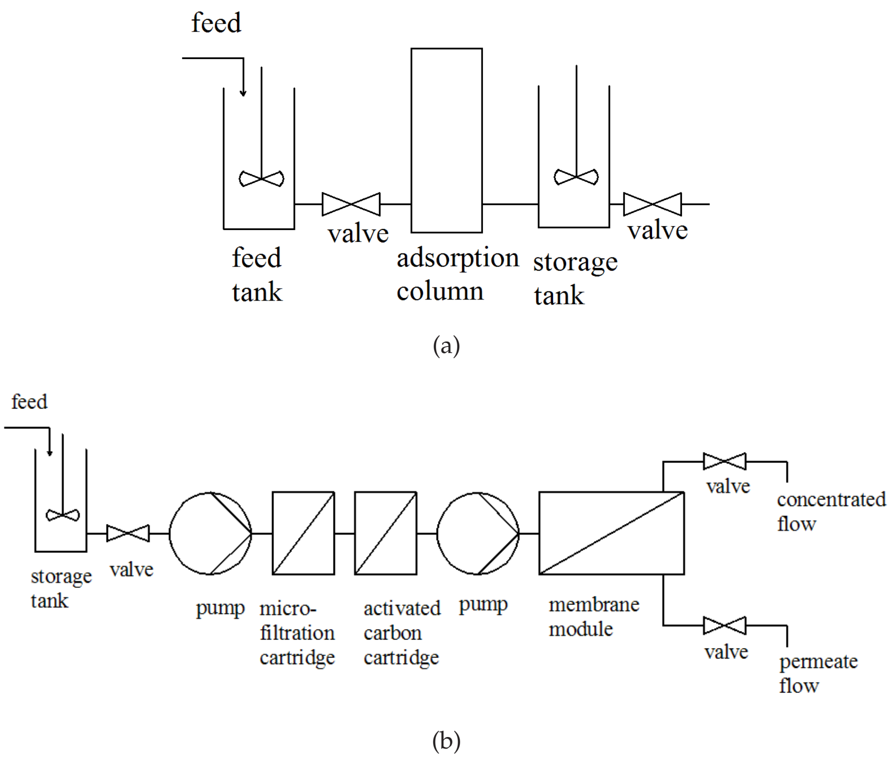

Fig. 1. Schematic figure of experimental set-up. a) Adsorption column b) Membrane filtration.

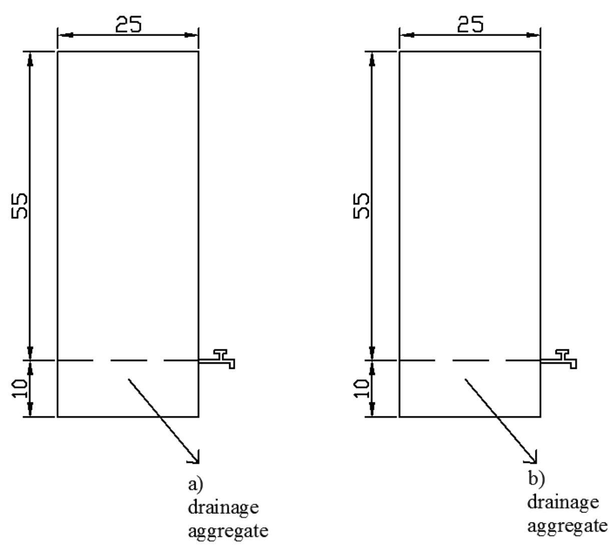

Fig. 2. Schematic figure of activated carbon column: Activated carbon column and b) Activated carbon-sand column.

3. Results and discussion

At the onset, three types of adsorption column were tested: activated carbon, activated carbon-sand with ratio of 2:1 and activated carbon-sand with ratio of 1:2, in order to establish the fact that which of 3 is the best in terms of removal efficiency. In the following,the combination of these methods with RO and NF membrane is tested. The results are as follows:

Table 4
Characteristic of activated carbon

Parameter	Range
Area, m^2/g	700–1300
Density, kg/m^3	400–500
Wet density, kg/l	1–1.5
Particle size, mm	1–2.36
Effective size, mm	0.9–0.6
Uniformity coefficient	<1.9
Ash, %	<8

Table 5
Comparison of activated carbon and sand gradation

Percent passing of sand	Percent passing of activated carbon	Sieve size (mm)
100	100	4.75
46.45	100	2.36
30.28	26.7	1.18
2.26	2.4	0.6
0.67	1	0.3
0.49	0.5	0.15
0.0	0.0	0.075

3.1. Activated carbon column

In this study, 50 L of effluent of waste water treatment with flow rate of 3 L/min passed through the activated carbon column, and the porosity of adsorbent is 0.69. The results are as follows:

Activated carbon column ability to remove TDS and EC is very negligible, but its removal efficiency in other parameters is acceptable, as depicted in Table 6.

3.1.1. Effects of different nitrate concentration on effluent of activated carbon column

In this case, three concentrations of nitrate were applied, by increasing the concentration of nitrate, removal efficiency of all parameters decreases, as depicted in Table 7.

3.2. Activated carbon-sand column with ratio of 2:1

Similarly, effluent of waste water treatment was passed through activated carbon-sand column with ratio of 2:1.The porosity of the mix adsorbent is 0.42. The system's ability to remove TDS and EC is not very considerable. But removal efficiency in other parameters is acceptable, as depicted in Table 8. In this test removal efficiency of all parameter has decreased, compared to the previous one,since the added sand increases only the porosity,not the adsorption process.

3.2.1. Effects of different nitrate concentration on effluent of activated carbon column-sand column with ratio of 2:1

The results showed that by increasing the concentration of nitrate, the removal efficiency of all parameters decreases, as depicted in Table 9.

3.3. Activated carbon-sand column with ratio of 1:2

Likewise, effluent of waste water treatment plant was passed through activated carbon-sand column with ratio of 1:2. The porosity of the mix adsorbent is 0.39. The system's ability to remove TDS and EC is very negligible and removal efficiency in other parameters decreased. According to Table 10, it was observed that by reducing the activated carbon and increasing standard sand, removal efficiency reduced, because the increase in sand functioned as a drainage system and served no adsorption role.

3.3.1. Effects of different nitrate concentration on effluent activated carbon-sand column with ratio of 1:2

As the results shown in Table 11 by increasing the concentration of nitrate, the removal efficiency of all parameters decreases.

3.4. Comparison among three previous tests

All systems remove a significant amount of nitrate, COD and TU, but the ability to remove TDS and EC is very insignificant as depicted in Fig. 3. By reducing the activated carbon and increasing the sand, the removal efficiency of all

Table 6
Removal efficiencies in activated carbon system

Parameter	Removal, %
EC	16.2
TDS	16
NO_3–N	76.8
PO_4–P	48.1
TU	93
COD	65.4

Table 7
Removal efficiency of different nitrate concentration on effluent of activated carbon column

	EC	TDS	NO_3–N	PO_4–P	TU
C_{NO3-N} = 90 mg/l	16.2%	16%	76.8%	48.1%	93%
C_{NO3-N} = 140 mg/l	15%	15%	74.1%	35.6%	92.3%
C_{NO3-N} = 190 mg/l	13.4%	13.2%	63%	30.4%	89%

Table 8
Removal efficiencies in activated carbon-sand column with ratio of 2:1

Parameter	Removal efficiency, %
EC	10.3
TDS	10.2
NO_3–N	69.8
PO_4–P	38.7
TU	84
COD	57.1

Table 9
Removal efficiencies of different nitrate concentration in activated carbon-sand column with ratio of 2:1

	EC	TDS	NO_3–N	PO_4–P	TU
C_{NO3-N} = 90 mg/l	10.3%	10.2%	69.8%	38.7%	84%
C_{NO3-N} = 140 mg/l	8.7%	8.7%	66.3%	23.5%	82.6%
C_{NO3-N} = 190 mg/l	6.4%	6.3%	45%	18%	79.2%

Table 10
Removal efficiencies in activated carbon-sand column with ratio of 1:2

Parameter	Removal efficiency, %
EC	8
TDS	7.9
NO_3–N	63.5
PO_4–P	32.7
TU	79.4
COD	45.4

Table 11
Removal efficiencies of different nitrate concentration in activated carbon-sand column with ratio of 1:2

	EC	TDS	NO_3–N	PO_4–P	TU
C_{NO3-N} = 90 mg/l	8%	7.9%	63.5%	32.7%	79.4%
C_{NO3-N} = 140 mg/l	6.3%	5.8%	55.9%	17.4%	75.9%
C_{NO3-N} = 190 mg/l	4.1%	3.7%	34.6%	11.8%	72.5%

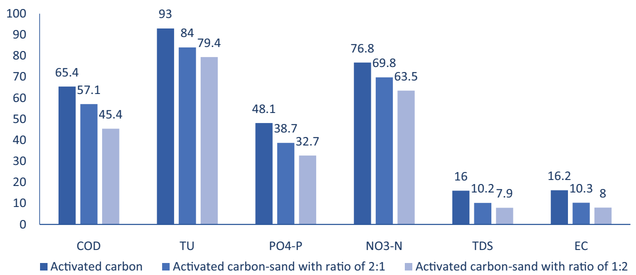

Fig. 3. Comparison of removal efficiency.

parameters decreased, yet this efficiency reduction is not to an extent that these systems cannot be used;from economic point, the activated carbon-sand with ratio of 1:2 is highly recommended.

3.5. RO membrane

In this approach, at a constant temperature and pH, 50 L of wastewater treatment plant effluent were passed through RO membrane. To reach the optimum pressure, several tests have been performed at different pressure as in the following:

3.5.1. Effects of pressure on effluent of RO membrane at constant PH

Pressure was the variable in membrane system and according to removal efficiency and also discharge rate, the optimum pressure was selected. In this occasion, four different pressures were applied. As depicted in Table 12, the removal efficiency of TDS, EC and nitrate at a pressure of 7 bar is the highest and the efficiency of phosphate removal at all pressures is almost the same. On the other hand, the removal efficiency of turbidity and also the permeate flow rate at pressure of 9 bar is higher than other pressures, as shown in Table 13. Considering the trivial difference of removal efficiency of TDS, EC and nitrate at pressures of 7 bar, the pressure of 9 bar is introduced as the optimal pressure.

3.5.2. Effects of nitrate concentration on effluent of RO at constant PH

At this stage, at an optimum pressure, the concentration of nitrate increased to the checked RO efficiency at high concentrations of nitrate. Three concentrations of 90, 140 and 190 mg/l of nitrate were applied. According to Fig. 4, it is understandable that as the initial concentration of nitrate increased, removal efficiency of all parameters decreased.

Table 12
Removal efficiency in RO membrane system at constant PH

	EC	TDS	NO_3–N	PO_4–P	TU	COD
Pressure 5 bar	94%	94%	84.1%	99.3%	80.9%	–
Pressure 7 bar	95.4%	95.4%	85.3%	99.3%	85%	–
Pressure 9 bar	93.4%	93.6%	80%	99.3%	88%	93.6%
Pressure 11 bar	87.2%	86.2%	78.1%	99.2%	79.5%	–

Table 13
Influence of pressure on discharge in RO system at constant pH and variable pressure

	$Q_{permeate}$ (lit/min)	$Q_{concentrated}$ (lit/min)	Q_{total} (lit/min)
Pressure 5 bar	2.5	23	25.5
Pressure 7 bar	3.5	14	14.5
Pressure 9 bar	5.1	6	11.1
Pressure 11 bar	6	0	6

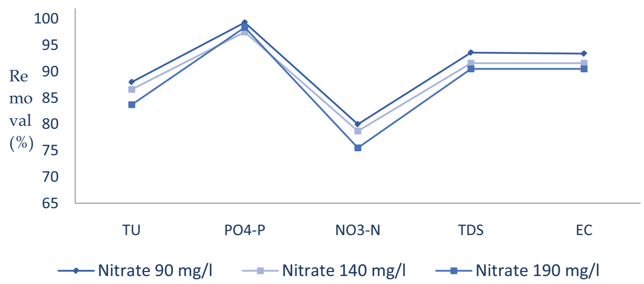

Fig. 4. Comparison of removal efficiency in RO with variation of initial concentration of nitrate at optimum pressure.

3.6. Activated carbon column as a pretreatment of RO membrane

Roughly similar, it can be said that, at constant temperature and pH, 50 L of wastewater treatment plant effluent were passed through RO membrane, thereby leading to activated carbon column. To arrive at the optimum pressure, several tests have been conducted, the results of which are depicted as in the following:

3.6.1. Effects of pressure on effluent of activated carbon column as a pretreatment of RO membrane at a constant PH

The optimum pressure was selected according to removal efficiency and also discharge rate. As shown in Table 14, the nitrate removal efficiency is the same at both pressures of 7 and 9 bar. On the other hand, the phosphate removal efficiency and TU are maximum at pressure of 9 bar and also the permeate flow rate at pressure of 9 bar is higher than pressure of 7 bar (Table 13), so the pressure of 9 bar is introduced as the optimum pressure.

Table 14
Removal efficiency in RO as a post-treatment of activated carbon column membrane system at constant PH

	EC	TDS	NO_3–N	PO_4–P	TU	COD
Pressure 5 bar	95%	95%	97.8%	98.2%	92.4%	–
Pressure 7 bar	97.3%	97.2%	98.9%	98.5%	93.3%	–
Pressure 9 bar	96.7%	96.5%	98.9%	99.3%	94.2%	95.2%
Pressure 11 bar	84.5%	84%	96.7%	99.3%	91.4%	–

3.6.2. Effects of nitrate concentration on effluent of RO as a post treatment of activated carbon at constant pH

Similarly, at an optimal pressure, the concentration of nitrate increased to the checked RO efficiency at high concentrations of nitrate. According to Fig. 5, it is understandable that as initial concentration of nitrate increased, removal efficiency of all parameters decreased. But it should be noted that with increasing concentration of nitrate, the efficiency of the whole parameter is almost 90%, and this is very desirable.

3.7. Activated carbon-sand column with ratio of 1:2 as a pre-treatment of RO

In this approach, two thirds of the column was filled with sand and one third with activated carbon. The effluent was, afterwards, exerted to RO system after passing through adsorbent column.

3.7.1. Effects of pressure on effluent of this system at a constant PH

The optimum pressure was selected according to removal efficiency and also discharge rate. As shown in Table 15, the removal efficiency of nitrate, EC and TDS at pressures of 5 and 7 bar is higher than pressure of 9 and 11 bar, and the highest efficiency is related to pressure of 7 bar. On the other hand, the removal efficiency of phosphate and turbidity at pressure of 9 bar is greater than 5 and 7 bar, but the difference in efficiency at the pressures of 7 and 9 bar is trivial. Also, the permeate flow rate at pressure of 9 bar is higher than other pressures. Therefore, according to the above and the importance of permeate flow; the pressure of 9 bar is an optimum pressure.

3.7.2. Effects of nitrate concentration on effluent of RO as a post-treatment of activated carbon-sand column with ratio of 1:2 at constant pH

At an optimal pressure, the concentration of nitrate increased to the checked RO efficiency at high concentrations of nitrate. Similarly as shown in Fig. 6, as initial concentration of nitrate increased, removal efficiency decreased, while this reduction was negligible for phosphate.

3.8. NF membrane

At a constant temperature and pH = 7.5, 50 liters of wastewater treatment plant effluent were passed through

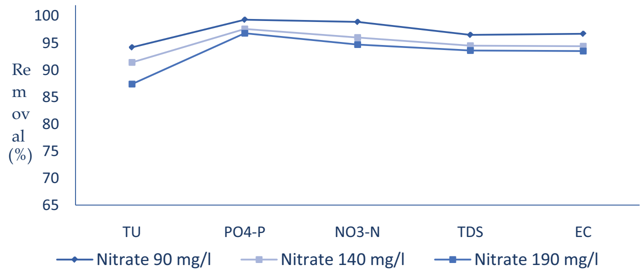

Fig. 5. Comparison of removal efficiency in RO as a post-treatment of activated carbon with variation of initial concentration of nitrate at optimum pressure.

Table 15
Removal efficiency in RO membrane as a post-treatment of activated carbon-sand column with ratio of 1:2

	EC	TDS	NO_3–N	PO_4–P	TU	COD
Pressure 5 bar	94.3%	94.3%	94%	97.7%	89%	–
Pressure 7 bar	94.8%	94.8%	94.5%	97.8%	90%	–
Pressure 9 bar	93.3%	93.4%	92.7%	99%	92.6%	94.1%
Pressure 11 bar	81.9%	81.4%	90.3%	98.1%	88.1%	–

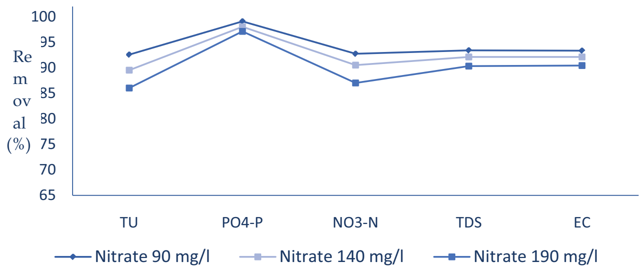

Fig. 6. Comparison of removal efficiency in RO system as a post-treatment of activated carbon-sand column with ratio of 1:2 with variation of initial nitrate concentration at optimum pressure.

NF membrane. To get the optimum pressure, several tests have been performed as in the following:

3.8.1. Effects of pressure on effluent of NF membrane at constant PH

According to removal efficiency and also discharge rate, the optimum pressure was selected. As shown in Table 16, the highest removal efficiency of TDS, EC, turbidity, nitrate and phosphate is related to pressure of 5 bar. The removal efficiency at pressure of 7 bar is also close to the removal efficiency of pressure of 5 bar, and on the other hand, the permeate flow at pressure of 7 bar is higher than the pressure of 5 bar, as shown in Table 17. Due to the importance of the permeate flow rate, the pressure of 7 bar was selected as the optimal pressure.

Table 16
Removal efficiency in NF membrane system at constant PH

	EC	TDS	NO_3–N	PO_4–P	TU	COD
Pressure 5 bar	84.3%	84.3%	70%	96.6%	87%	–
Pressure 7 bar	85.1%	85.3%	70.3%	98.4%	91.4%	–
Pressure 9 bar	77.4%	77.4%	68.9%	98.1%	89.9%	89.3%
Pressure 11 bar	68.7%	68.5%	67.4%	96.9%	80.8%	–

Table 17
Influence of pressure on discharge in NF system at constant pH and variable pressure

	$Q_{permeate}$ (L/min)	$Q_{concentrated}$ (L/min)	Q_{total} (L/min)
Pressure 3 bar	4.8	30	34.8
Pressure 5 bar	7.5	18	25.5
Pressure 7 bar	9.8	6.5	9.8
Pressure 9 bar	10.8	0	10.8

3.8.2. Effects of nitrate concentration on effluent of NF at constant PH

At an optimal pressure, the concentration of nitrate increased to checked NF efficiency at high concentrations of nitrate. Three concentrations of 90, 140 and 190 mg/l of nitrate were applied, and the results of which are shown in Fig. 7. According to Fig. 7, it is understandable that as the initial concentration of nitrate increased, removal efficiency of all parameters except phosphate decreased. This inconsistency results from a test error.

3.9. Activated carbon as a pretreatment of NF membrane

In the same vein, effluent of wastewater treatment plant was passed through activated carbon adsorbent column at a constant temperature and pH = 7.5 and then exerted to NF membrane. Pressure was considered as the variable in NF membrane. The optimum pressure was chosen according to removal efficiency and flow rate; therefore, COD experiment was run at an optimum pressure.

3.9.1. Effects of pressure on effluent of this system at a constant PH

The optimum pressure was selected according to removal efficiency and also discharge rate. As depicted in Table 18, the highest removal efficiency occurred at pressure of 5, which is due to the fact that the difference in removal efficiency is trivial at different pressures and also because of the high rate of permeate flow at pressure of 7 bar relative to pressure of 5 bar, as shown in Table 17, so pressure of 7 bar was considered as an optimal pressure.

3.9.2. Effects of nitrate concentration on effluent of RO as a post-treatment of activated carbon at constant pH

Similarly, in NF approach, three concentrations of 90, 140 and 190 mg/l of nitrate were applied and the results are

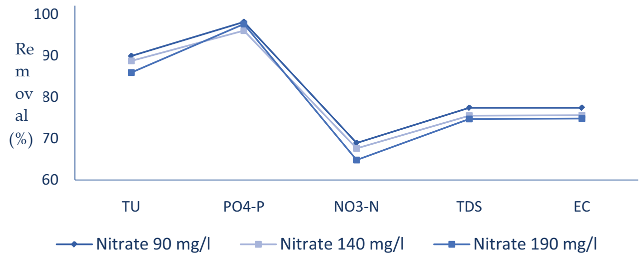

Fig. 7. Comparison of removal efficiency in RO with variation of initial concentration of nitrate at optimum pressure.

Table 18
Removal efficiency in NF membrane along with pre-treatment of activated carbon

	EC	TDS	NO_3–N	PO_4–P	TU	COD
Pressure 3 bar	90.8%	91%	96%	98%	96.5%	–
Pressure 5 bar	91.6%	91.6%	96.5%	99.3%	98%	–
Pressure 7 bar	87.7%	87.7%	95.4%	98.8%	96%	90.4%
Pressure 9 bar	74.4%	74.5%	94.1%	97.9%	90.2%	–

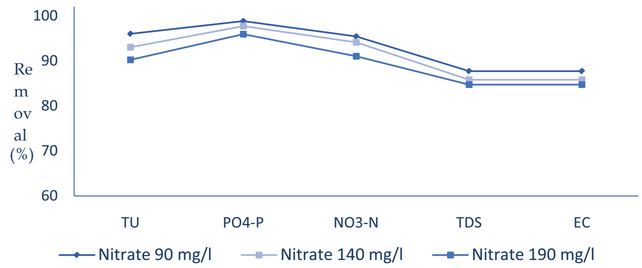

Fig. 8. Comparison of removal efficiency in NF as a post-treatment of activated carbon with variation of initial concentration of nitrate at optimum pressure.

shown in Fig. 8. In NF system, as the initial concentration of nitrate increased, the removal efficiency of all parameters decreased.

3.10. Activated carbon-sand column with ration 1:2 as a pre-treatment of NF

Two thirds of column were filled with sand and one third with activated carbon. The effluent of treatment plant was passed through activated carbon-sand column, and then exerted into NF membrane.

3.10.1. Effects of pressure on effluent of this system at a constant PH

According to removal efficiency and also discharge rate, the optimum pressure was selected. In this situation, four different pressures were applied. As shown in Table 19, the removal efficiency of TDS, EC and nitrate at pressure of 5 bar and phosphate and turbidity at pressure of 7 is the high-

Table 19
Removal efficiency of NF membrane as a post-treatment of activated carbon-sand column

	EC	TDS	NO_3–N	PO_4–P	TU	COD
Pressure 3 bar	86.2%	86.3%	87.7%	98.6%	91.8%	–
Pressure 5 bar	86.7%	86.7%	89.4%	98.9%	92.4%	–
Pressure 7 bar	81%	81.1%	88.3%	99.3%	94.7%	89.9%
Pressure 9 bar	71.7%	71.9%	86.6%	99%	89%	–

est. Given the close efficiency of the system in these two pressures, and also due to the high rate of permeate flow at pressure of 7 bar, pressure of 7 bar is considered as an optimal pressure.

3.10.2. Effects of nitrate concentration on effluent of NF as a post-treatment of activated carbon-sand column with ratio of 1:2 at constant pH

According to Fig. 9, it can be understood that as the initial concentration of nitrate increased, removal efficiency of all parameters except phosphate decreased.

3.11.Comparing the results of the membrane and combination of membranes with adsorbent column

In this section, an analogy is drawn between the two systems:

3.11.1. Comparison of removal efficiencies of RO and NF membrane

The removal efficiency of phosphate in both systems is roughly the same, but removal efficiency of TDS, EC, COD and nitrate in RO is higher than that of NF, while in terms of removal efficiency of TU, NF membrane is slightly better than RO (Fig. 10).

3.11.2. Comparison between removal efficiencies of combination of RO and NF membranes as a post-treatment of activated carbon column

As seen in Fig. 11, the removal efficiency of phosphate was similar for both membrane types. In terms of turbidity, NF membrane was more efficient. On the other hand, removal efficiency of other parameters was better in RO method.

3.11.3. Comparison between removal efficiencies of combination of RO and NF membranes with activated carbon-sand column with ratio of 1:2

The removal efficiency of the phosphate in both systems is almost the same, but the removal efficiency of TDS, COD, EC and nitrate in the combined system of RO is greater than the NF membrane. On the other hand, the function of the combined system of NF is better in removing TU (Fig. 12).

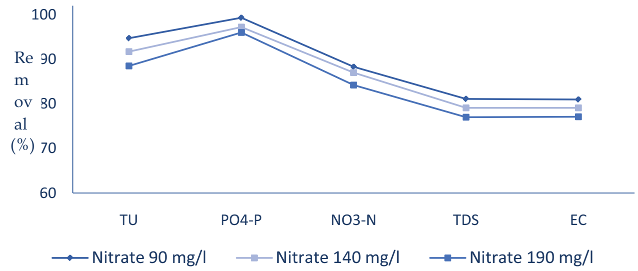

Fig. 9. Comparison of removal efficiency in NF as a post-treatment of activated carbon-sand with variation of initial concentration of nitrate at optimum pressure.

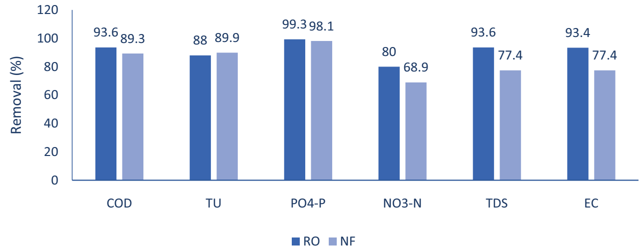

Fig. 10. Comparison between removal efficiency in RO and NF membrane.

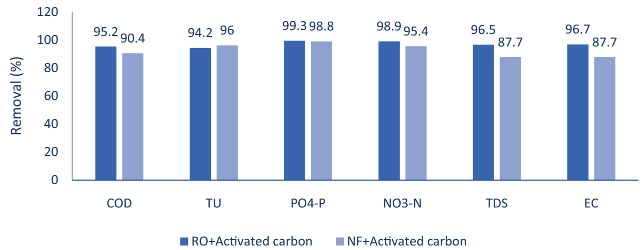

Fig. 11. Comparison between removal efficiency of RO and NF membrane as a post-treatment of activated carbon.

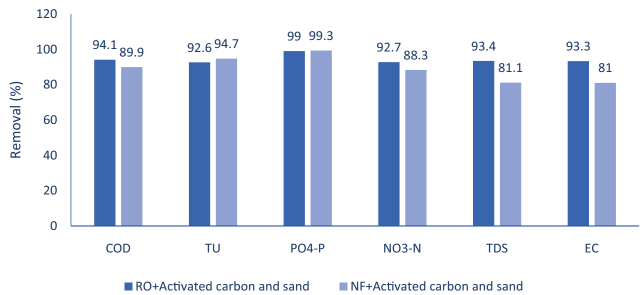

Fig. 12. Comparison between removal efficiency of RO and NF systems as a post-treatment of activated carbon-sand column at optimum pressure and constant pH.

4. Conclusion

In this study, activated carbon column, activated carbon-sand column with ratio of 2:1 and activated carbon-sand column with ratio of 1:2, remove a significant amount of nitrate, COD and TU, but the ability to remove TDS and

EC is very insignificant. As the concentration of nitrate increased the removal efficiency of nitrate, phosphate and COD in RO membrane, activated carbon as pre-treatment of RO and activated carbon-sand column with ratio of 1:2 as a pre-treatment of RO decreased. By reducing activated carbon and increasing sand, the removal efficiency of all parameters decreased, but this efficiency reduction is not to an extent that these systems cannot be used, from an economic point the activated carbon-sand with ratio of 1:2 is highly recommended. Experiments were administered at different pressures. Optimum pressures for RO and its combination with adsorption column was 9. As the concentration of nitrate increased the removal efficiency of nitrate and COD in NF and activated carbon-sand column with ratio of 1:2 as a pre-treatment of NF decreased. Removal efficiency of activated carbon as a pre-treatment adsorption column was much higher in comparison with activated carbon-sand as a pre-treatment of adsorption column. The highest removal efficiency was obtained in RO as a post-treatment of activated carbon column. Removal efficiency of nitrate, phosphate and COD were 98.9%, 99.3% and 95.2%. In order to reach an economic method, the amount of activated carbon should be removed, so RO, as a post treatment of activated carbon-sand column with ratio of 1:2 is recommended, removal efficiency of nitrate, phosphate and COD was 92.7%, 99% and 94.1%, respectively. Optimum pressures for NF and its combination with adsorption column was 7 bar. Removal efficiency of nitrate, phosphate and COD in NF system along with activated carbon was 95.4%, 98.8% and 90.4%. In order to reach an economic method, we recommend NF as a post treatment of activated carbon-sand column with ratio of 1:2 in which removal efficiency of nitrate, phosphate and COD was 88.3%, 99.3% and 89.9% respectively.

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