REMOVAL OF CHROMIUM FROM WASTES OBTAINED FROM CHROMIUM-COATING APPLICATION BY USING REVERSE OSMOSIS WITH AG, SWHR AND SE MEMBRANE

ABSTRACT

The removal of chromium from waste water obtained from chromium-coating application was investigated by using reverse osmosis (RO) technique using FILMTEC SWHR (sea water high rejection) and GE OSMONICS AG and SE (high rejection brackish water) membranes. The effect of pH, concentration of the feed water and operating pressure on the chromium rejection was also investigated. Chromium rejection was dependant on membrane type, pH of the feed water and operating pressure. pH of feed water was found 3 to be optimum effective removal of chromium. The rejection efficiency of the membranes was found to be in the order of AG > SWHR > SE. For all membranes, chromium rejection increased with operating pressure. RO could be efficiently used (with >91% rejection) for the removal of chromium from liquid waste sample.

Keywords: Chromium Removal, Reverse Osmosis, Membrane, pH, AG

AG, SWH AND SE MEMBRANLARLA, TERS OZMOZ KULLANILARAK, KROM KAPLAMA UYGULAMALARINDAN ELDE EDİLEN ATIK SUDAN KROM UZAKLAŞTIRMASI

ÖZET

Krom kaplama uygulamalarından elde edilen atık sudan krom giderimi FILMTEC SWHR (deniz suyu yüksek reddetme), GE ozmonics AG ve SE (yüksek reddetme acı su) membranlar kullanılarak ters ozmoz (RO) metoduyla araştırıldı. Krom reddetmesi üzerine pH'nın, besleme suyunun konsantrasyonun ve işlem basıncının etkisi araştırıldı. Krom reddetmesi membran tipine, besleme suyunu pH'sına, işlem basıncına bağlıdır. Besleme suyunu pH'sı etkili krom uzaklaştırması için yaklaşık olarak 3 bulunmuştur. Membranların reddetme etkisi; AG > SWHR > SE şeklindedir. Bütün membranlar için krom reddetmesi işlem basıncıyla artar. Ters ozmoz metodu, sıvı atık numuneden krom çıkarımı için etkili(%91'den büyük)bir şekilde kullanılır.

Anahtar Kelimeler: Krom Uzaklaştırma, Ters Ozmoz, Membrane, pH, AG

1. INTRODUCTION (GİRİŞ)

Water pollution by heavy metals is one of the major economic and environmental issues in various parts of the world [1]. Among these heavy metals, chromium (Cr) is a common contaminant in surface water and ground water resulting from numerous industrial activities such as the preservation of wood, textile dyeing, leather tanning, electroplating and metal finishing [2]. The chromium element exists mainly in the Cr (III) and Cr (VI) valence states, although Cr (0), Cr (II), and Cr (V) have also been observed. Common Cr (VI) anions, chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) are strong oxidants and chromate is known to be carcinogen and a suspected mutagen and teratogen. By contrast, Cr (III) toxicity is negligible because it often forms insoluble hydroxides at circum-neutral pH [3]. Accordingly, chromium containing waste waters must be treated to lower the Cr (VI) to allowable limits before discharging into the environment. Conventional methods utilized to remove the Cr (VI) from industrial waste waters include reduction followed by chemical precipitation [4], activated carbon adsorption [5], electrochemical precipitation [6], ion exchange [7], solvent extraction [8], reverse osmosis [9], etc. These processes apart from being economically expensive have certain disadvantages like high reagent and energy requirements, incomplete metal removal, and generation of a large quantity of toxic waste sludge, which necessitates careful disposal in further steps [10]. Recently, a search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial by products, as potential metal adsorbents. The variety of materials tested as Cr (VI) adsorbents includes algae [11], charcoal, wool, olive cake, sawdust, pine needles, almond shells, cactus leaves [12], rice husk [13], crushed coconut shell, peat moss, exhausted coffee, waste tea, moulds, yeast, bacteria, crab shells, soybean hulls and cottonseed hulls, hazelnut shell, wheat bran's, sawdust, mustard seed cakes, bark and straw [14].

Johns et al. [15] utilized granular activated carbons (GACs) made from walnut hull compared to commercial GACs in order to successfully remove higher levels of benzene, toluene, methanol, acetonitrile, acetone and 1,4-dioxane from an aqueous mixture.

The treatment methods used for the removal of chromium from water can be divided into several categories like coagulation and electrocoagulation processes [16 and 17], adsorption [18 and 19], ion-exchange processes [20 and 21] and membranes processes such as Donnan dialysis [22], electrodialysis [23] and RO) [24 and 25].

In recent years, membrane manufactures have developed RO membranes with chromium rejections of 91-96% [26 and 27]. However, most of the current desalination plants have to implement the additional treatment steps such as pH adjustment of feed water, post-treatment of RO permeate with ion exchange or several pass stage of permeate in order to improve chromium rejection. In addition, several process configurations have been proposed to obtain the low chromium concentration of thepermeate from RO plant [21, 28 and 29].

The RO membranes produced by FILMTEC Co offered advantages over traditional cellulose acetate (CA) RO membranes. The most important of these advantages were better rejection of dissolved solids and organics, increased productivity at lower operating pressures, great structural stability, and the ability to produce two to three times more purified water per unit area than CA membranes. Furthermore, these membranes combine higher flux efficiency with a larger area packaged in the same volume and format as conventional 8 inch elements allowing for a substantial reduction of investment costs, as well as

lower operating costs due to reduced pressure and fouling tendency. In the case of the low energy consuming elements, the part of the operating cost related to energy consumption has been roughly reduced by 30 to 50% compared with conventional RO membranes [30]. Additionally, application of antiscalants is not required when FILMTEC SWHR membrane was used in RO system at high pH values [31]. Based on these advantages, FILMTEC RO membranes were efficiently used for the removal of boron [31 and 32], silica [32] and salt [33 and 34] from water. The removal of chromium by RO is affected by several factors, i.e., pH, pressure, feed flow rate, initial concentration, etc. Therefore, it is critical to find out a relationship between % removal of chromium and affecting parameters and to optimize the RO process. The previous works indicate that each parameter shows the similar effect on chromium removal regardless of membrane used. Generally, the effect of pH and pressure on chromium removal by RO membranes is important while initial chromium concentration is negligible [31, 35, 36 and 37].

The present study was designed to investigate and compare the chromium removal efficiencies of three different RO membranes (AG, SWHR, and SE) using model solutions containing chromium as single solute. The effect of pH and concentration of feed water and operating pressure on the chromium rejection was also investigated.

2. RESEARCH SIGNIFICANCE (ÇALIŞMANIN ÖNEMİ)
The impotant of study: Many methods have been tried to remove chromium from waste water [2, 4 and 7] but the method of removal of chromium from waste water by using reverse osmosis is more detailed than the other methods. This method was used to remove boron [18], arsenate and arsenide [38] from water. In terms of reliability, reproducibility, affordability and originality, this method is superior to other methods. Removal of chromium with AG membrane is 96%.

3. MATERIALS AND METHODS (MATERYAL VE METOD)
3.1. Reverse Osmosis Pilot Plant (Ters Ozmoz Pilot System)
The reverse osmosis pilot plant (Prozesstechnick GmbH) used in this study consists of a diaphragm pump controlled with a frequency converter (1.8-12 L/min flow range and pressure range of max 40 bar), feed tank with heating/cooling jacket (5 L capacity), membrane housing for both spiral wound and flat-sheet membranes, different emptying and pressure valves (Fig. 1).

3.2. Membranes (Membranlar)
Three different types of membranes (44 cm^2 exposed area) used in this study along with their relevant characteristics are summarized in Table 1.
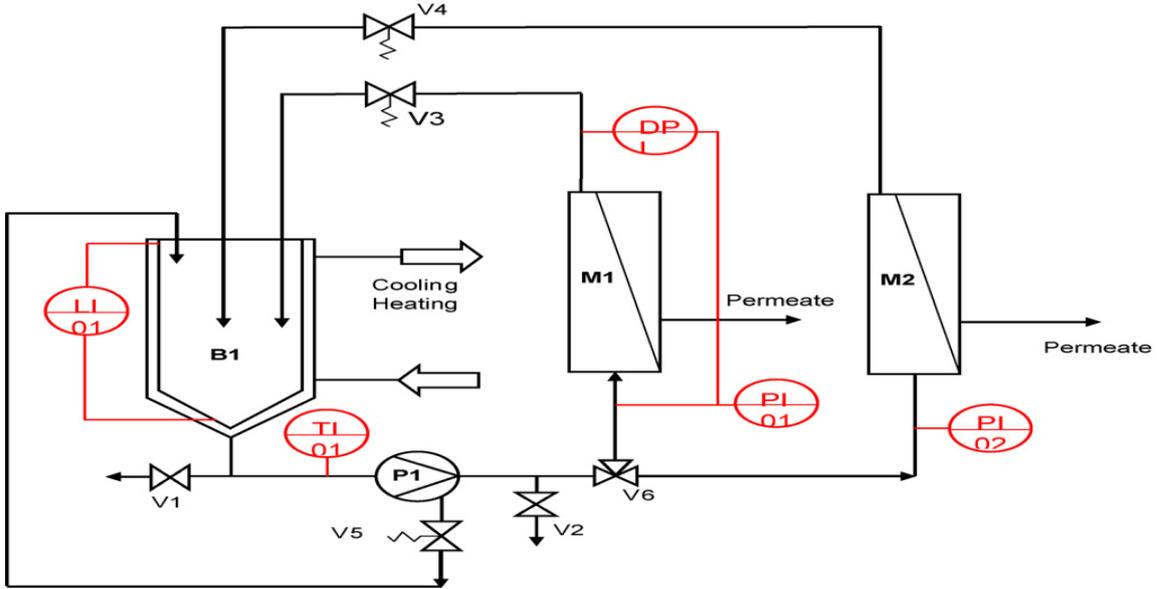
Figure 1. Flow diagram of the reverse osmosis plot plant (M1 and M2: Membrane housing, B1: Feed tank with heating/cooling jacket, V1 and V2: Emptying valve, V3 and V4: Pressure regulation valve, V5: Spring loaded valve, V6: Three way valve to select which membrane housing, P1: Pump, PI01 and PI02: Pressure gauge, DP1: Differential pressure indicator, LI01: Level indicator on the feed tank, TI01: Temperature indicator) [18].
(Şekil 1. Ters ozmoz plot sistemin akış diagramı (M1 ve M2: Membran koyulacak yer, B1: Isıtma/ soğutma ceketli besleme tankı, V1 ve V2: Boşaltma valfi, V3 ve V4: Basınç düzenleme valfi, V5: Yüklenen valf, V6: Membran evini seçmek için üç yollu valf, P1: Pompa, PI01 ve PI02: Basınç ölçer, DP1: Diferansiyel basınç göstergesi. LI01:Besleme tankı üzerinde seviye göstergesi, TI01: Sıcaklık göstergesi)))

Table 1. Characteristics of the membranes used
(Tablo 1. Kullanılan membranların özellikleri)

	Membranes (membranlar)		
Characteristics (özellikler)	SWHR	AG	SE
Configuration	Flat-sheet	Flat-sheet	Flat-shat
Max temperature (°C)	45	50	50
Max pressure (psig)	1200	600	800
Salt rejection (%)	99.6	99	98
Chlorine tolerance (ppm)	< 0.1	1000	500

3.3. Experiments (Deneyler)

The potassium dichromate solutions were prepared in distilled water by diluting the prepared stock solutions (1 mg/mL) to desired concentrations. $K_2Cr_2O_7$, NaOH and HCl were obtained from Merck Co. (Darmstadt, Germany). All chemicals were the analytic grade reagents. Composition of the feed water and operating pressure in experiments, were chosen as below:

- 50, 100, 500 and 1000 mg/L Chromium solution at pH= 5.5 and operating pressure of 20 bar.
- 100 mg/L chromium solution at pH ranging from 1 to 6 and operating pressure of 20 bar.
- 100 mg/L chromium solution at pH= 1 at 15 to 35 bar operating pressure.

pH of the feed water (1 L) was adjusted to the desired pH level by using 0.1M NaOH or 0.1M HCl and was placed in the feed water tank. The system was operated in the permeate recycle mode. A new membrane was used for each experiment after conditioning the membrane at least 3 h under the experimental conditions. The measuring sequence was determined by taking permeate sample after each hour and their chromium concentrations were taken. The experiments were performed at 20±1°C. The chromium rejection was calculated according to the equation (1):

Chromium rejection (%) = [1- ($C_{permeate}$ / C_{feed})] x 100   (1)

Where $C_{permeate}$ and C_{feed} are the chromium concentrations of thepermeate and feed water, respectively.

3.4. Liquid Waste Sample Obtained from Chromium-Coating Application (Krom Kaplama Uygulamalarından Elde Edilen Sıvı Atık Numune)

The application of RO on the liquid waste sample from Chromium-coating application from Konya, Turkey was performed under optimal conditions. (20^0C temperature, 15, 20, 25, 30, 35 bar pressure, 1-6 pH and 50, 100, 500 and 1000 mg/L concentrations)

3.5. Instruments (Aletler)

The concentration of chromium and cations in the samples was determined by ContraAA 300 Atomic Absorption Spectroscopy (ContraAA 300, Analytikjena). The wavelength utilized for the determination of chromium was 357 nm. Linearity for chromium was observed in the concentration range of 10-1000 mg/L. In addition, coefficient of regression (R^2) and limit of detection (LOD) for chromium were 0.999 and 2.935 mg/L, respectively. pH of the samples was determined by an Orion ion meter with combined pH electrode.

4. RESULTS AND DISCUSSION (SONUÇLAR VE TARTIŞMA)
4.1. Effect of Feed Water Concentration (Besleme Suyu Konsantrasyonunun Etkisi)

The results on effect of feed water concentration on the chromium rejection showed in significant effect (Fig 2). Permeate water concentration increased with increase in feed water concentration in AG membrane but showed declining effect with SWHR, AG and SE membranes (Fig. 3). Results showed that chromium rejection is not dependant on the feed concentration [39]. Results further showed the clear impact of membrane type and pH on chromium rejection (Fig. 2) and support the findings of Dydo et al. [24]. Chromium % rejection for membranes was found to be in the order AG > SWHR > SE. The highest rejection was obtained by using AG membrane, whereas the lowest rejection was observed for SE membrane. The mean rejections for AG, SWHR and SE membranes were 95.762, 92.845 and 85.820, respectively, Dydo et al. [24]. These results showed that chromium rejection evidently depends upon membrane type.
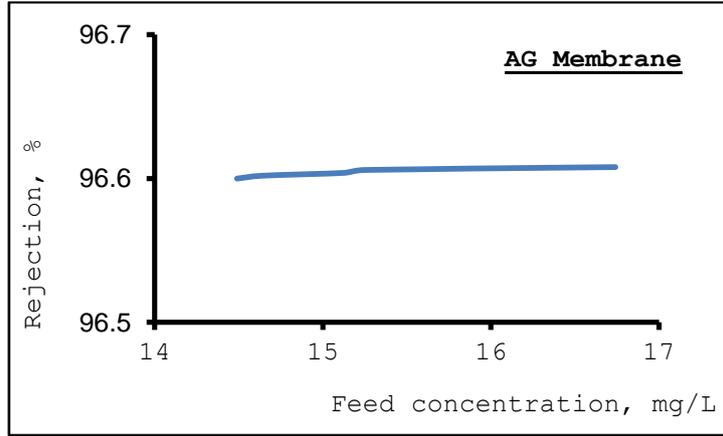
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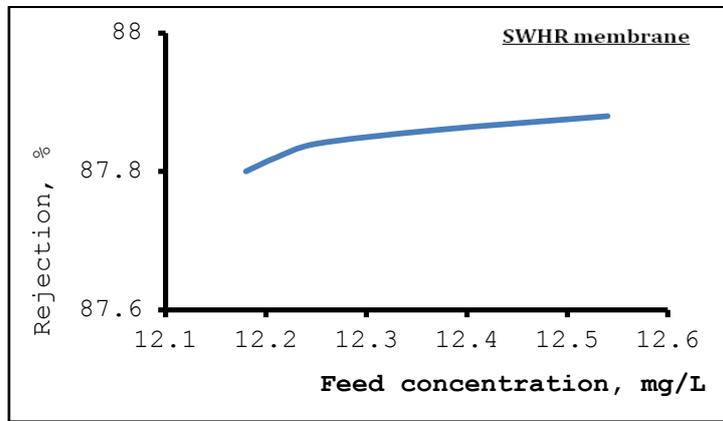
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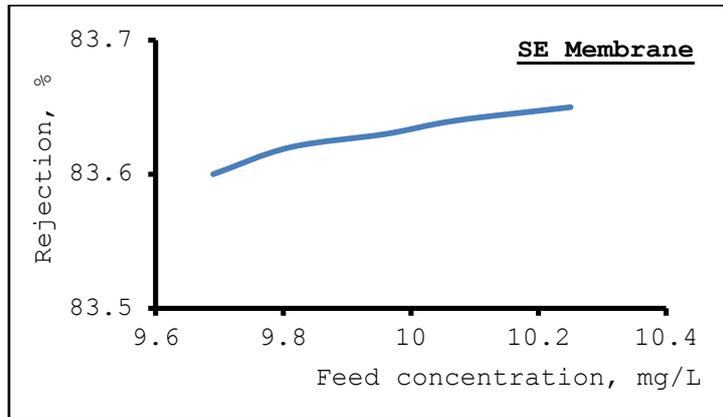
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Figure 2. Dependency of chromium rejection on the chromium
concentration of feed water. pH of feed water: 5.5, operating
pressure: 20 bar, temperature: 20 °C. Dependency of chromium rejection
on the chromium concentration of feed water for AG, SWHR and SE
membranes respectively is given fig a b c.
(Şekil 2. Krom reddetmesinin besleme suyundaki krom konsantrasyonuna
bağlılığı. Besleme suyunun pH'ı: 5.5, işlem basıncı:20 bar, sıcaklık:
20^0C. Krom reddetmesinin, besleme suyunun krom konsantrasyonuna
bağlılığı AG, SWHR ve SE membranlar için sırayla şekil a, b ve c'de
verilmiştir)
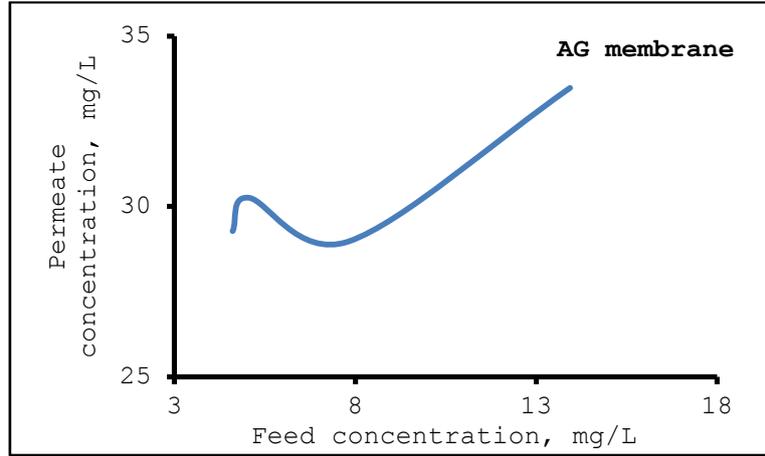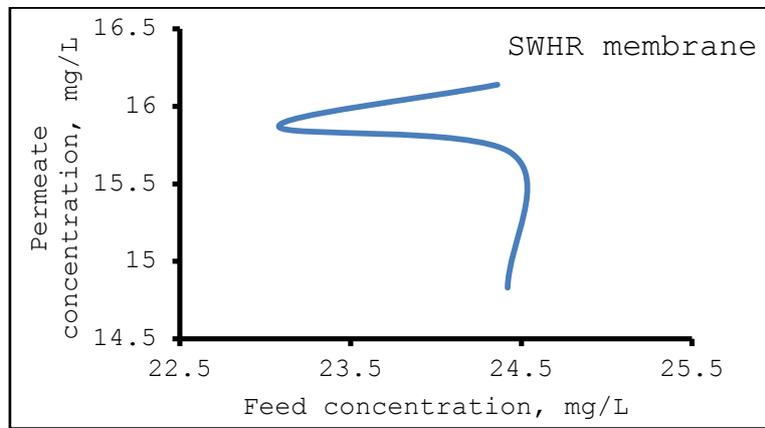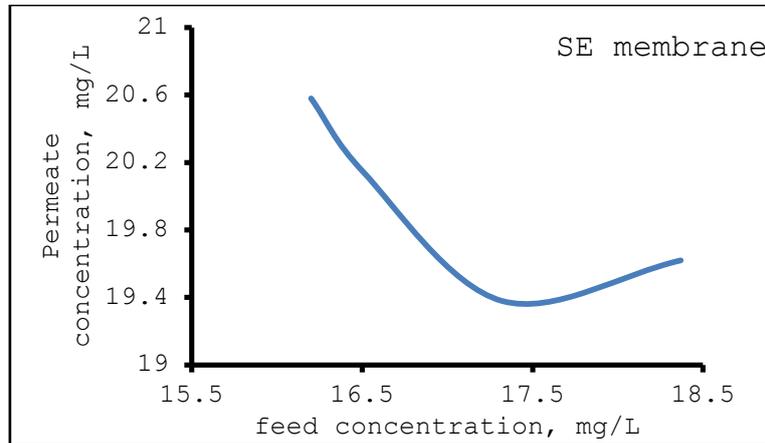
Figure 3. Dependency of permeate concentration on the chromium
concentration of feed water. pH of feed water: 5.5, operating
pressure: 20 bar, temperature: $20^{o}C$. Dependency of permeate
concentration on the chromium concentration of feed water for AG, SWHR
and SE membranes respectively is given fig. a.b.c.
(Şekil3. Permeate konsantrasyonunun besleme suyundaki krom
konsantrasyonuna bağlılığı. Besleme suyunun pH'ı: 5.5, işlem basıncı
:20 bar, sıcaklık: $20^{0}C$. Permeate konsantrasyonunun besleme suyunun
krom konsantrasyonuna bağlılığı AG, SWHR ve SE membranlar için sırayla
şekil a, b ve c'de verilmiştir)

4.2. Effect of pH of Feed Water
(Besleme Suyunun pH'sının Etkisi)

Earlier studies have shown that solution pH is an important parameter influencing the biosorption of metal ions [2 and 11]. Chromium (VI) removal was investigated as a function of solution pH and the result is indicated in Fig. 4. for AG, SWHR and SE membranes. As seen from this figure, chromium rejection is strongly dependent upon pH of the feed water. For all studied membranes, an increase in the chromium rejection was observed with increases of pH of the feed water. The highest chromium rejection was obtained at pH = 3. Chromium % rejection for membranes was found to be in the order AG > SWHR > SE with highest rejection was obtained by using SWHR membrane and the lowest rejection was observed for SG membrane. The mean rejections for AG, SWHR and SE membranes were 92.933, 86.418 and 84.160, respectively.

The distribution of the Cr (VI) species in solution depends on pH and Cr (VI) concentration in the following form [40]:

$$H_2CrO_4 \quad \overset{\log K = 0.382}{\leftrightarrow} \quad HCrO_4^- \quad \overset{\log K = -6.14}{\leftrightarrow} \quad CrO_4^{2-}$$
$$\updownarrow \quad \log K = 1.706$$
$$Cr_2O_7^{2-}$$
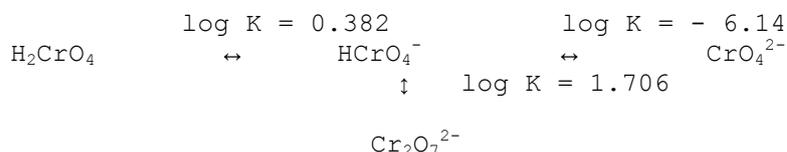
Therefore at low pH values, the dichromate and acid chromate ion species were predominant in solution. In the presence of a reducing substrate, these species are quickly converted according to the following equations [40 and 41].

$$3\ CxOH + Cr_2\ O_7^{2-} + 4H^+ \leftrightarrow 3CxO + HCrO_4^- + Cr^{3+} + 3H_2O$$
$$3\ CxOH + HCrO_4^- + 4H^+ \leftrightarrow 3CxO + Cr^{3+} + 4H_2O$$

Where CxO represents the oxo groups of the sorption sites Chromium (III) ions remained in solution at pH= 1.0 and for a chromium (VI) initial concentration of 100 mg/L the concentration of the $Cr_2O_7^{2-}$ could be assumed negligible in the adsorption process [40 and 41]. Hence only the acid chromate ion species ($HCrO_4^-$) could be adsorbed on the protonated active sites of the biosorbent substrate. A decrease in adsorption above pH= 3.0 may also be related to the occupation of the adsorption sites by anionic species like CrO_4^{2-}, CrO_7^{2-}, etc., which retard the approach of such ions further towards the sorbent surface [42 and 43]. In the following experiments, the highest chromium rejection was obtained at pH = 3 (Fig. 4).
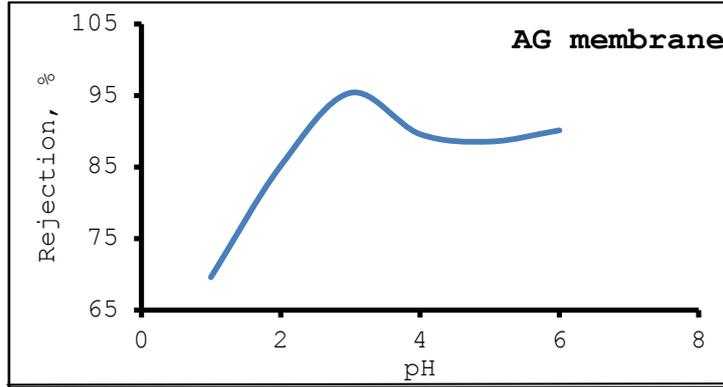
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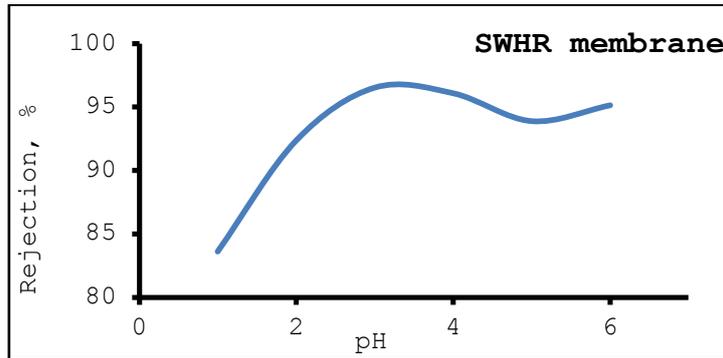
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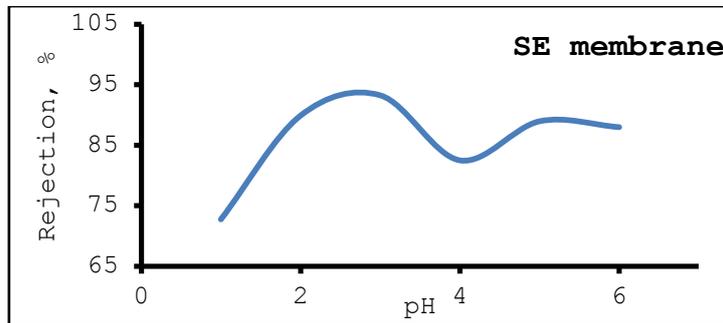
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Figure 4. Dependency of chromium rejection on pH of feed water. Chromium concentration of feed water: 100 mg/L, operating pressure: 20 bar, temperature: $20^{o}C$. Dependency of chromium rejection on pH of feed water for AG, SWHR and SE membranes respectively fig. a, b, c. (Şekil 4. Krom reddetmesinin besleme suyunun pH'ına bağlılığı. Besleme suyunun krom konsantrasyonu: 100 mg/L, işlem basıncı:20 bar, sıcaklık: $20^{0}C$. Krom reddetmesinin besleme suyunun pH'ına bağlılığı AG, SWHR ve SE membranlar için sırayla şekil a, b ve c de verilmiştir)

4.3. Effect of Operating Pressure (İşlem Basıncının Etkisi)

Chromium rejections for AG, SWHR and SE membranes increased with increasing operating pressure (Fig 5). Similarly, Koseoglu et al. [25], Sutzkover et al. [44] and Prats et al. [45] reported that higher chromium rejection was observed when operating pressure was increased. Chromium % rejection for membranes was found to be in the order of AG> SWHR > SE. The highest rejection was obtained by using SWHR membrane, whereas the lowest rejection was observed for AG membrane. The mean rejections for AG, SWHR and SE membranes were 84.986, 79.099 and 72.110, respectively.
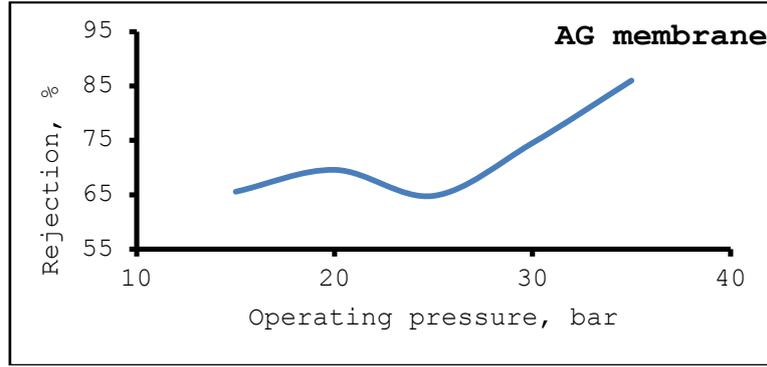
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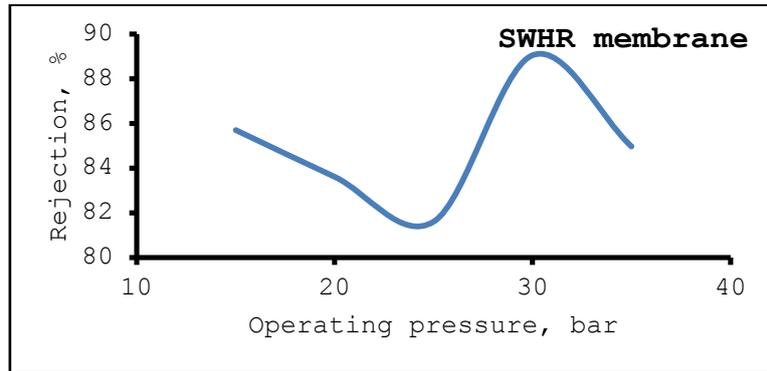
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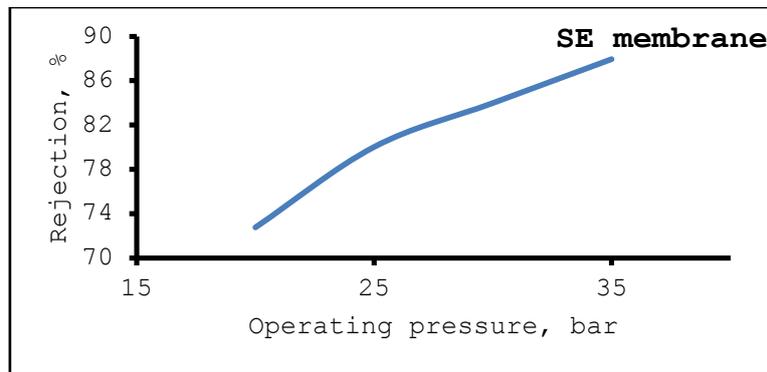
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Figure 5. Dependency of chromium rejection on the operating pressure. Chromium concentration of feed water: 100 mg/L, pH of feed water: 5.5, temperature: 20°C. Dependency of chromium rejection on the operating pressure for AG, SWHR and SE membranes respectively is given fig. a.b.c.
Şekil 5. Krom reddetmesinin işlem basıncına bağlılığı. Besleme suyunun krom konsantrasyonu: 100 mg/L, işlem basıncı :20 bar, sıcaklık:20^{0}C. Krom reddetmesinin işlem basıncına bağlılığı AG, SWHR ve SE membranlar için sırayla şekil a, b ve c'de verilmiştir).

In addition, operating pressure also increased permeate flux (Fig. 6) and was found in the order AG > SWHR> SE. Higher operating pressure resulted in higher volume of permeate water. The same observation was indicated by Koseoglu et al. [25]. Permeate flux is important because higher flux gives the short operation time, which reduces the cost of RO system.
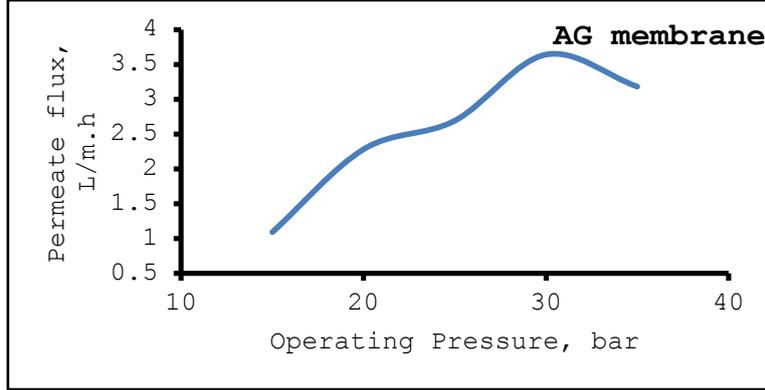
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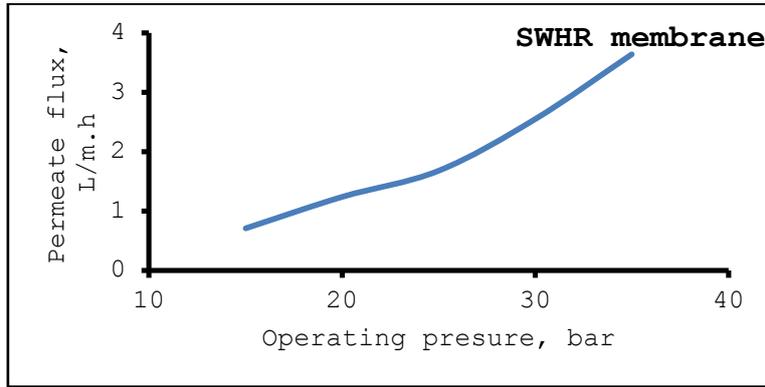
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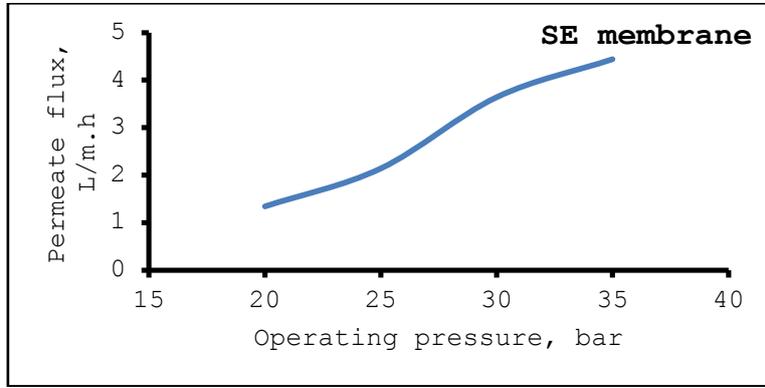
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Figure 6. Dependency of permeate flux on the operating pressure.
Chromium concentration of feed water: 100 mg/L, pH of feed water: 5.5,
temperature: 20 °C. Dependency of permeate flux on the operating
pressure for AG, SWHR and SE membranes, respectively is given fig.
a.b.c.
(Şekil 6. Permeate akışın işlem basıncına bağlılığı. Besleme suyunun
krom konsantrasyonu: 100 mg/L, işlem basıncı:20 bar, sıcaklık:20^{0}C.
Permeate akışın işlem basıncına bağlılığı AG, SWHR ve SE membranlar
için sırayla şekil a, b ve c'de verilmiştir).

4.4. Waste Water Obtained from Chromium-Coating Application
(Krom Kaplama Uygulamalarından Elde Edilen Atık Su)

The highest rejection and permeate flux were obtained by using AG membrane (chromium % rejection: AG > SWHR> SE, permeate flux: AG > SWHR> SE). And was used for the removal of chromium from waste water obtained from chromium-coating application by RO technique. Waste water was taken from Konya (Turkey) with chromium concentrations of 100 mg/L. Prior to RO application, pH of the waste sample was adjusted to 3 at which the highest chromium rejection was obtained. Fig. 7 shows the time dependence of chromium rejection for waste water. The mean chromium rejections for AG, SWHR and SE were recorded as 97%, 87% and 74% respectively. It increased with increase in time in AG and SE membrane whereas it reduced with increase in time in SWHR (Fig. 7). Results further showed that fluxes for sample reached a steady state values with increased permeate fluxes (Fig. 8). Permeate fluxes for sample were recorded as 4.6 –13.9 L/m^{2}h.
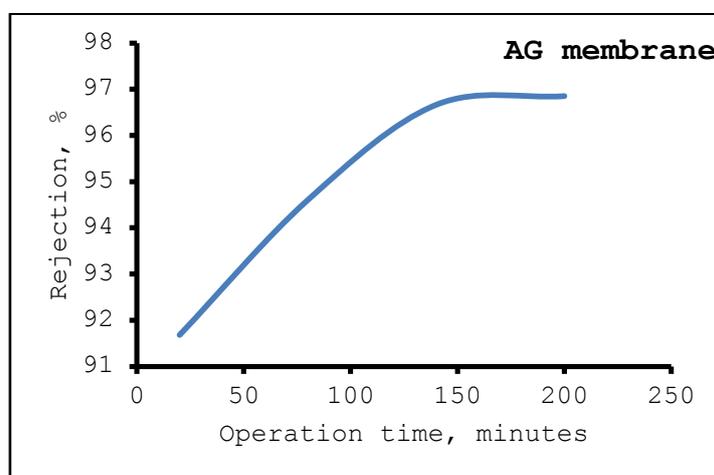
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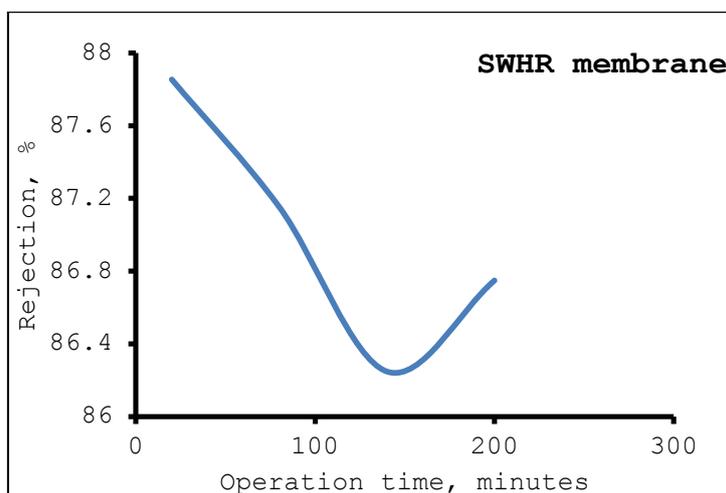
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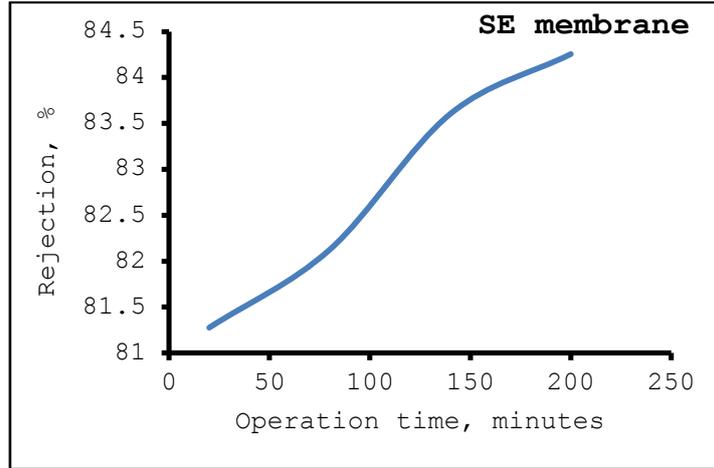
(c)

Figure 7. Dependency of chromium rejections on operating time. Chromium concentration of waste sample obtained from chromium-coating applications: 7542 mg/L,pH of feed water: 5.5, operating pressure: 20 bar, temperature: 20 °C. Dependency of chromium rejections on operating time for AG, SWHR and SE membranes respectively is given fig. 7.a.b.c. (Şekil 7. Krom reddetmesinin işlem zamanına bağlılığı. Krom kaplama uygulamalarından elde edilen atık numunenin krom konsantrasyonu: 7542 mg/L, besleme suyunun pH'ı:5.5, işlem basıncı : 20 bar, sıcaklık: 20 °C. Krom reddetmesinin işlem zamanına bağlılığı, AG, SWHR ve SE membranlar için sırayla şekil a, b ve c'de verilmiştir).
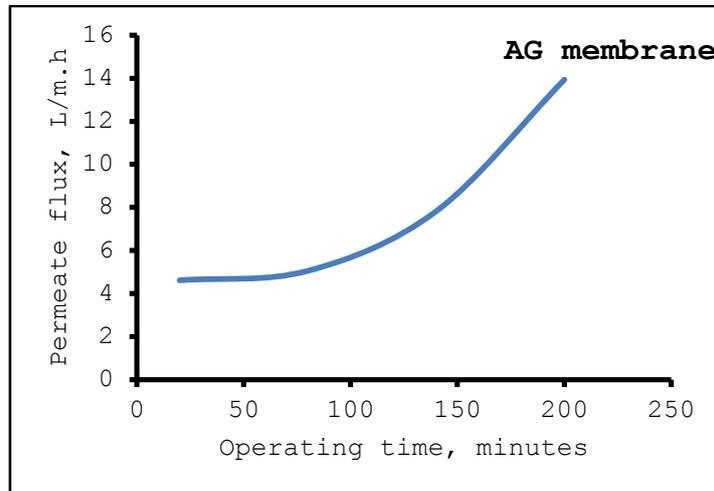
Figure 8. Permeate fluxes for natural samples.Waste sample obtained from Chromium-coating applications was 7542 mg/L, pH of feed water: 6.01, operating pressure: 20 bar, temperature: 20 °C , for AG membrane. (Şekil 8. AG membranda doğal numuneler için pemeate akışlar. Krom kaplama uygulamalarından elde edilen atık numune 7542 mg/L, besleme suyunun pH'ı: 6.01, işlem basıncı:20 bar, sıcaklık:20 °C).

The chemical composition of the waste waste was determined by three times analyses [n = 3] and the results are given in Table 2.

Table 2. The chemical composition of the waste water obtained from chromium-coating application
(Tablo 2. Krom kaplama uygulamalarından elde edilen atık suyun kimyasal bileşimi)

Ionic species (iyonik türler)	Concentration, mg/L (n = 3)
Cd	0.1946
Cr	7542
Cu	76
Fe	828.6
Ni	1.55
Pb	48.6
Zn	5.813

WHO requires that chromium concentration in drinking water is below 0.5 mg/L. In addition, EU (European Union) defines the limit concentration of in drinking water as 1 mg/L. These requirements have affected the RO process design because of difficulty in achieving such low chromium concentrations. In order to overcome this problem, additional steps such as dilution of RO permeate with other sources, ion exchange post-treatment of RO permeate, and/or double-pass have been employed by most of the desalination plants [24 and 46]. For example, Dydo et al. [24] reported that high chromium rejection (close to 96%), and low permeate concentration (<1 mg/L) were obtained at pH = 3 by single stage RO with AG membrane. Therefore, they proposed a two-stage RO system (at pH = 3) to efficiently remove the chromium from waste water.

5. CONCLUSION (SONUÇ)

The present study presents the comparison of different RO membranes, pH, concentration and operating pressure on chromium rejection. It can be concluded that removal of chromium by RO depends greatly on the pH of the feed water and pH = 3 is found to be optimum for all membranes to remove chromium effectively. Removal of chromium increases with increasing the operating pressure. Whereas the rejection of chromium does not depend upon the feed water concentration. Waste water obtained from chromium-coating application containing 7542 mg/L of chromium were treated by using RO with AG membrane and obtained results showed that RO could be efficiently used (with > 91% rejection) for removal of chromium from waste water [47].

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