**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY**

# EFFECTS OF SUSPENDED AND BLENDED SILVER NANOPARTICLES ON FILTRATION PERFORMANCES AND BACTERIAL PRODUCTS AT MEMBRANE BIOREACTOR (MBR) SYSTEM

**M.Sc. THESIS**

**Saliha BESLEN**

**Department of Environmental Engineering**

**Environmental Biotechnology Programme**

**MAY 2014**

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**MAY 2014**

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**Date of Submission : 30 May 2014**
**Date of Defense : 29 May 2014**

## FOREWORD

The membrane processes have been increasingly used for drinking water and wastewater treatment. At recent years, it can seen that the silver nanoparticles have been widely used for increasing the filtration performances. Inthisthesiswork, theeffects of suspended and blended silvernanoparticles on filtration performance, bacterial products and wastewater treatment performance at membrane bioreactor (MBR) were determined with short and long term experiments.

I will first and foremost like to thank my great supervisor Prof. Dr. İsmail KOYUNCU for giving me very good back-up and advices. I would like to express my great appreciation to Assoc. Prof. Dr. Derya Y. İMER for his scientific guidance and valuable discussions.

I would like to acknowledge TUBITAK (The Scientific and Technological Research Council of Turkey) (Project No: 111Y095) for financially supporting the research described in this thesis.

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## ABBREVIATIONS

| | |
|---|---|
| **AgNP** | **:** Silver Nanoparticle |
| **EPS** | **:** Extracellular Polymeric Substances |
| **MLSS** | **:** Mixed Liquor Suspended Solids |
| **NPs** | **:**Nanoparticles |
| **PES** | **:** Polyethersulfone |
| **SMP** | **:** Soluble Microbial Products |

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**EFFECTS OF SUSPENDED AND BLENDED SILVER NANOPARTICLES ON FILTRATION PERFORMANCES AND BACTERIAL PRODUCTS AT MEMBRANE BIOREACTOR (MBR) SYSTEM**

## SUMMARY

The membrane filtration systems have now become an attractive option for the water and wastewater treatment and reuse of industrial and municipal wastewaters. However, the filtration performance inevitably decreases with time due to membrane fouling. After more than 10 years of intensive research, consensuson the exact fouling phenomena in MBRs has not been reached yet.There are lots of factors affecting the membrane fouling, but these factors can be categorized based on membrane material properties, sludge characteristic and operating conditions.The last membrane fouling studies have concerned with the modification of membrane material for anti-biofouling. This modification can providewith the addition of nanoparticles (NPs) in the production of polymeric membrane. Especially,silver nanoparticle (AgNP) which is incorporated into polymeric membrane via blending was used commonly for preventing membrane fouling due to its antimicrobial property.However, released silver ions ($Ag^+$) from nanocomposite membrane may have effects on MBR performance adversely.

Also, the usage of silver nanoparticles cause nanoparticles to enter sewage pipes and the wastewater treatment plants (WWTPs). However, the impact that nanoparticles have on wastewater treatment, is largely unknown and studies on inhibition of microbial growth by silver nanopaticles in wastewater treatment systems are limited.

This study focuses on identifying relationships between blended and suspended silver nanoparticles and membrane filtration performance, bacterial products and wastewater treatment performance. Experiments were performed in two different stages. Firstly, the effects of short-term suspended silver nanoparticle exposure at different concentrations on filtration performance and bacterial products were determined. In the first step of short-term, different exposure times were studied at constant concentration. In the second step of short-term, different concentration were studied at constant exposure time.Secondly, effects of silver nanoparticle exposure were investigated at the long-term. For this,the lab-scale MBR were conducted at three different operation periods. At first operation period, the bare PES membrane in flat sheet module was used as control for compare with other periods.At second operation period,the silver nanocomposite PES (AgNP-PES) membrane was used for blended form of silver nanoparticle. In the third operation period, the bare PES membrane was used and 10 mg AgNP/L was added to mixed liquor of the MBR on daily basis.In the long-term exposure, not only suspended silver nanoparticle but also blended silver nanoparticle was used and their effects on filtration performance, bacterial products and wastewater treatment performance were evaluated.

**MEMBRAN BİYOREAKTÖRLERDE ASKIDA VE MEMBRANDA TUTUKLU GÜMÜŞ NANOPARÇACIKLARIN FİLTRASYON PERFORMANSI VE BAKTERİYEL ÜRÜNLERE OLAN ETKİLERİ**

## ÖZET

Membran Biyoreaktör (MBR) teknolojisi, aktif çamur sayesinde sağlanan biyolojik arıtımın ve membran filtrasyonunun bir arada kullanıldığı bir atıksu arıtma teknolojisidir. Evsel ve endüstriyel atıksu arıtımında deşarj standartlarının daha sıkı uygulanması MBR uygulamalarının tercih edilmesine neden olmaktadır. Fakat MBR uygulamalarının kullanılmasındaki en büyük sorun membran kirlenmesidir. Son yıllarda literatürde membran sistemleri ile ilgili olarak birçok çalışma yapılmıştır. Kirlenme, membran yüzeyinin veya gözeneklerinin askıda katı maddeler, partiküller veya kolloidler tarafından kontrolsüz bir şekilde tıkanmasıdır. İçme suyu veya doğal sularda kullanılan membran sistemlerinde, kirlenmeye kolloidal maddeler sebep olurken, atıksu arıtımında özellikle aktif çamur sistemine entegre edilen membran sistemlerinde (membran biyoreaktör-MBR) kirlenmeye hem bakteriyel hücreler hem de hücre dışına salgılanan kolloidal maddeler sebep olmaktadır. MBR sistemlerinde ayırımı gerçekleştirilecek olan süspansiyonun canlı materyaller içermesi kirlenme problemini daha da zorlaştırmaktadır. Membranların biyolojik olarak kirlenmesinin incelendiği birçok çalışmada, kirlenme problemini etkileyen faktörler üç ana başlık altında toplanmıştır; besi-biyokütle özellikleri, işletme şartları ve membran özellikleri. Biyokütle ve besi özelliklerinin etkisinin incelendiği çalışmalarda özelikle bakteriler tarafından üretilen hücre dışı çözünmüş (SMP veya sEPS) veya bağlı (bEPS) polimerik materyallerin ana kirleticiler olduğu tespit edilmiştir. Dolayısıyla bu başlık altında yürütülen çalışmalar, genellikle giriş atıksuyunun özellikleri ile bakterinin ürettiği bu ürünler arasındaki ilişkiyi temel almaktadır. İşletme şartlarının incelendiği çalışmalarda ise çamur yaşı (SRT), havalandırma hızı veya hidrolik bekletme süresinin (HRT) etkileri incelenmiştir. Bu çalışmalar kirlenme mekanizmasının belirlenmesi açısından önemli bilgiler vermiştir. Ancak kesin sonuçlara varmak zordur. Çünkü değişen reaktör şartlarında kirlenmeye neden olan parametreler de değişiklik göstermektedir. Bunun yanında büyük ölçekli kullanımlarda özellikle işletme şartlarını değiştirmek diğer başka problemlere sebep olmaktadır. Membran özelliklerinin incelendiği çalışmalar bu iki başlık altında gerçekleştirilen çalışmaların yanında oldukça az sayıdadır. Çünkü ticari olarak MBR sistemlerinde kullanılacak olan membran tipleri oldukça kısıtlıdır ve bu membran tipleri ile de çalışmalar gerçekleştirilmiştir. Ancak, yapısı nedeniyle bazı polimerlerin doğal hidrofobisiteleri düşük membran akısı ve çabuk tıkanma özellikleri nedeniyle uygulama ve faydalı ömrü üzerinde büyük bir etkiye sahiptir. Membran özellikleri hakkında az sayıda çalışma yapılmıştır çünkü membranlar ticari membran türleri sınırlı kalmış ve bu membranlar birçok çalışmalada kullanılmıştır.Son membran kirlenme çalışmaları, membralara düşük tıkanma özellikleri kazandırmak için membran malzemesinin fiziksel veya kimyasal modifikasyonunu içermektedir.Son membran kirlenme çalışmaları kirlenme önleyici özellikler kazandırmak için membran malzemesinin fiziksel veya kimyasal modifikasyonu üzerinedir. Bu çalışmalar üç ana başlıkta toplanabilir; fiziksel ve kimyasal işleme ile membran yüzey modifikasyonu, yeni malzemeler ekleyerek membran üretimi, düşük kirlenme özellikleri için spacer kullanarakmembran kaplaması.Şimdiye kadar membran modifikasyon çalışmaları yararlı sonuçlar vermiştir.Bu

nedenle, bu çalışmanın temel amacı nanomalzemeler ile membran üretimi ve bu membranların karakterizasyon deneylerinin ardından filtrasyon performanslarının belirlenmesidir.

Son 1-2 yılda kirlenme ile ilgili çalışmalar membran materyalinin özelliklerinin kirlenmeyi önleyecek şekilde modifiye edilmesine doğru yönelmiştir. Bu konuda yapılan çalışmalarda kendi içinde bölümlere ayrılmıştır. Bunlar, ticari membranların yüzey özelliklerinin fiziksel veya kimyasal yöntemler ile değiştirilmesi ve membran yüzeyinin çeşitli ara malzemeler ile kaplanması ve çeşitli ek maddeler ile membran üretimidir. Şu ana kadar membran özelliklerinin değiştirilmesi ile ilgili yapılan bu çalışmalar olumlu sonuçlar vermiştir. Bu noktadan hareketle, nanoteknoloji alanındaki gelişmelere bağlı olarak polimerik membran üretiminde nanoparçacık kullanımı son yıllarda özellikle akının iyileştirilmesi ve tıkanmanın önlenmesi konularında oldukça önem kazanmıştır. Polimerik membran sentezi sırasında boyutları 4-100 nm arasında değişen nanoparçacık ve nanotüp ekleme girişimlerinin başarılı olduğu literatürdeki birçok çalışmada belirtilmektedir. Bu nanomateryallerin tıkanmanın azalmasında, süzüntü suyu karakterinin iyileşmesinde ve akının artmasında çok önemli rol oynadıkları bildirilmiştir. Titanyum, alumina, silika, gümüş, zeolit, demir ve karbon nanotüp gibi nano materyaller en çok tercih edilen malzemelerdir.Nanopartiküller birçok farklı maddeden, elementel kompozisyonu, şekli, boyutu, fiziksel ve kimyasal özellikleri değişim göstererek, çeşitli fiziksel ve kimyasal metotlarla sentezlenebilirler. Nanoboyutta maddelerin özellikleri yığın formuna göre belirgin şekilde değişim gösterir. Maddenin boyutu küçüldükçe atom yüzey alanı artar, bu da reaktifliği arttırır ve yüzeydeki atomlar basit katalitik proseslerin aktif merkezleri olmasıyla yüksek reaktif katalistler haline dönüşürler. Böylece nanopartiküller nanometre ölçeği boyutunda benzersiz elektronik, optik, manyetik ve mekanik özellikler gösterirler. Bu benzersiz özellikleri sebebiyle nanopartiküller kataliz, atıksu arıtımı, tekstil, boya, ilaç iletimi, manyetik rezonans görüntüleme (MRI), doku mühendisliği ve kanser tedavisi alanlarında kullanılmaktadır. Farklı tipteki nanopartiküllere son yıllarda hem sanayi hem de akademik çalışmalarda yoğun şekilde odaklanılmıştır. Nanopartiküller çok küçük boyutlardaki hacimlerine göre geniş yüzey alanları sebebiyle çok reaktiftirler. Yüksek reaktivite potansiyeli, nanopartiküllerin biyolojik sistem ve çevreyle zararlı ilişkisine bağlı olarak toksisiteye sebep olma potansiyeline sebep olabilmektedir.

Özellikle gümüş sahip olduğu antimikrobiyal özellikten dolayı polimerik membran üretiminde yaygın şekilde kullanılır oldu. Çünkü bu antibakteriyel etki, gümüşün bakteriyel proteinin yapısında bulunan thiol grupları ile reaksiyona girerek elektron taşıma zincirine ve DNA'nın yapısına zarar vermesinden kaynaklanmaktadır. Aynı şekilde virüslerin yapısına da zarar verirler. Gümüş nanoparçacıklar, selüloz asetat, poliimid, poliamid gibi membranlar ile birlikte laboratuar ölçeğinde üretilmiştir. Membranın polimer matrisinin yapısına katılarak membrana anti bakteriyel özellik kazandırdığı belirtilmiştir. Bu sayede membran üzerinde oluşan çamur kekinin oluşmasının engellendiği görülmüştür. Polisülfon ile ilgili olarakta birkaç çalışma yapılmıştır. Fakat gümüşün membran yapısındaki mekanizması tam olarak belirlenememiştir. Özellikle, uzun süreli ve gerçek çamur ortamında performans çalışmaları henüz yapılmamıştır. Bu tez çalışması kapsamında da uzun süreli ve gerçek çamur ortamında içinde gümüş nanopartikül (AgNP) bulunduran polietersülfon (PES) polimerik malzemeyle üretilmiş düz plaka membranlar kullanılmış ve membranın fitrasyon performansını belirlemenin yanısıra atıksu arıtım performansını da belirlenmiştir. Çünkü atıksu ortamında membran tıkanma problemini azaltmak için kullanılan AgNP-PES kompozit membranlardan aktif çamurun bulunduğu atıksuya gümüş iyonu ($Ag^+$) salınmaktadır ve bu gümüş iyonu gümüş nanomateryal gibi antimikrobiyal özelliğe sahiptir. Dolayısıyla MBR'deki aktif çamurun aktivitelerini olumsuz etkileyebilirler. Bu yüzden bu tez çalışmasında AgNP-PES kompozit membrandan olası salınacak gümüş iyonunun MBR aktif çamurunun üzerine olan etkilerini dışarıdan PES polimerik malzemeyle üretilmiş düz plaka membran kullanıldığı biyoreaktöre ilave edilen gümüş nanopartiküller ile karşılaştırılarak belirlenmesi amaçlanmıştır.

Ayrıca bu dışarıdan gümüş nanopartikül ilave edilmesiyle çalıştırılan MBR nanomateryallerdeki kullanım artışı, nanopartiküllerin kasıtlı/kasıtsız olarak kanalizasyon ve atıksu arıtma tesislerine girmesiyle ilişkilendirilmektedir. Çünkü atıksu arıtımının nanomateryaller üzerindeki etkileri veya bunun tersi nanomateryallerin atıksu arıtım tesisi üzerindeki etkileri bilinmemektedir. Dahası, bu maddelerin endüstriyel veya evsel atıksu arıtma tesislerinden verimli uzaklaştırılmasının yolu konusunda da soru işaretleri vardır. Son çalışmalar nanopartiküllerin atıksu arıtma sisteminde tutulamadığını ve doğal su ortamlarına deşarj edildiğini göstermektedir. Bu nanopartiküller doğada uzun süre kalmakta ve su yaşamında potansiyel toksik etki göstermektedir. Nanopartiküller yayıldıkları zaman, elektrostatik ve van der Waals etkileşimleri ile sulak yüzeylerle etkileşmekte ve biyolojik türlerle birleşmektedir. Bu sebepten dolayı, atıksu arıtma tesisleri ve atıksu çamurundaki nanopartiküllerin olası davranış ve zararları üzerine yeni analiz yöntemleri gerekmektedir. Bu çalışmada askıda ve membranda tutuklu gümüş nanopartiküllerinin membran filtrasyon performansı, bakteriyel ürünler ve atıksu arıtma performansı arasındaki ilişkileri belirlenmesi üzerinde durulmuştur.Deneyler iki farklı aşamada yürütülmüştür. Öncelikleksa süreli askıda gümüş nanopartiküllerin filtrasyon performansı ve bakteriyel ürünlere olan etkileri farklı konsantrasyonlarda belirlenmiştir. Kısa süreli maruziyetin ilk adımında sabit gümüş konsantrasyonunda farklı maruziyet süreleri denenmiş, ikinci aşamada ise sabit maruziyet süresinde farklı konsantrasyonlar denenmiştir. Kısa süreli maruziyetin etkilerinin belirlenmesinden sonra uzun sureli maruziyetin etkileri araştırılmıştır. Bunun için laboratuar ölçekli MBR üç farklı periyodda işletilmiştir. İlk periyodda MBR'a saf PES düz plaka membran modülü daldırılmıştır ve bu periyod diğer periyodlar için kontrol olarak işletilmiştir.İkinci periyodda gümüş nanopartikülün membran içinde tutuklu formu yani AgNP-PES kompozit membran kullanılmıştır. Üçüncü periyodda ise gümüş nanopartikülün askıda formu kullanılmıştır. Bunun için tekrar saf PES membran kullanılmış ayrıca hergün 10mg/L gümüş nanopartiküller eklenmiştir. Böylelikle uzun süreli askıda ve membranda tutuklu gümüş nanopartikül maruziyetinin membran filtrasyon performansı, bakteriyel ürünler ve atıksu arıtma performansı üzerine olan etkileri belirlenip değerlendirilmiştir.

## 1. INTRODUCTION

Membrane bioreactors (MBRs) are being increasingly used for municipal and industrial wastewater treatments for high removal efficiency or high effluent quality. Membrane bioreactor technology combines the biological degradation process by activated sludge with a direct solid–liquid separation by membrane filtration. The solid–liquid separation leads to keeping much more microorganisms in the bioreactor. Consequently, MBRs have high concentrations of mixed liquor suspended solids (MLSS), low production of excess sludge and small bioreactor requirements. Hence, the MBR systems have many advantages over conventional wastewater treatment systems. However, the membrane fouling is the most important obstacle to membrane development. Because it worsens membrane filtration performance and shortens membrane life. The membrane fouling in MBRs can be attributed to both membrane pore plugging and sludge cake deposition on membranes. There are lots of factors affecting the membrane fouling, but these factors can be categorized based on membrane material properties, sludge characteristic and operating conditions. The membrane fouling is inevitable, but it can be controlled. For instance, the properties of membrane materials can be modified by the addition of nanoparticles (NPs) in the production of polymeric membrane. NPs are being used due to unique properties in the many fields and a modification of the surface chemistry and morphology of the membranes by using NPs can increase the membrane filtration performance. Especially, silver nanoparticles (AgNPs or nanosilver) are being incorporated in polymeric materials in the membrane fabrication because nanosilver has strong antimicrobial activities to inhibit bacterial growth and sludge cake formation on the surface of the membrane.Nonetheles, AgNP releases silver ions ($Ag^+$) in the aqueous state; thus, effects of $Ag^+$ on suspended microorganisms should take into consideration due to biological activity in the MBR. Because silver ions have antimicrobial property like AgNPs.

On the other hand, there is a concern about the potential impact of AgNPs in wastewater treatment systems because of their increasing usage. AgNPs from nanotechnology-enhanced products are discharged to the sewage pipes and conveyed to wastewater treatment plants (WWTPs). MBR technology has been increasingly using in WWTPs;

therefore, AgNPs in the mixed liquor of the MBR can affect suspended microorganisms adversely depending on its concentration owing to toxic effect of AgNPs or the membrane fouling might be reduced by affecting attached bacteria on the membrane Hence, the effects of AgNP should investigate in terms of membrane filtration performance, bacterial products and treatment performance as both blended and suspended in the MBR.

## 1.1 Purpose of Thesis

The main objective of this study is to investigate effects of long-term suspended and blended silver nanoparticles exposure on membrane bioreactor (MBR) activated sludge. This study was carried out in three different MBR operation periods and silver nanoparticle was used at the different forms in these periods. One of these forms is silver nanoparticle which is incorporated into polymeric membrane via blending and these composite membranes may release silver ions ($Ag^+$). Effects of this possible releases on filtration performance, bacterial products and wastewater treatment performance was aimed to investigate by comparing effects of silver nanoparticle which added to mixed liquor of the MBR.

## 1.2 Scope of Thesis

In this thesis study, effects of silver nanoparticle exposure were investigated at the short and long terms. Firstly, the effects of short-term suspended silver nanoparticle exposure at different concentrations on filtration performance and bacterial products were determined. Short-term suspended silver nanoparticle exposure was conducted two stages. In the first stage, different exposure times were studied at the same silver nanoparticle concentration for selection of the best suitable exposure time. In the second stage, different silver nanoparticle concentrations were studied at the same exposure time selected according to results of first stage experiments. Secondly, MBR was operated with the purpose of long-term exposure. In the long-term exposure, not only suspended silver nanoparticle but also blended silver nanoparticle was used and their effects on filtration performance, bacterial products and wastewater treatment performance were evaluated.

# 2. LITERATURE REVIEW

## 2.1 Definition of Nanoparticles

The word ‘Nano’ derived from the Greek word “nanos”, which means dwarf or extremely small. The nanoscale (1 nm = $10^{-9}$ m) is a billionth of a metre. Generally dimensions of nano particles ranges from 0,1-100 nm. A nanometre(nm) is one billionth of a metre, or roughly the length of three atoms kept side byside. A DNA molecule is 2.5 nm wide, a flu virus about 100 nm and human hairis approximately 10,000 nm thick. A nanoparticle is a microscopicparticle with at least one dimension less than 100 nm. Nano-sized particles have large surface areas relative to their volumes and thus have enhanced chemical and biological reactivity. Owing to their small dimensions nanoparticles can be tailored possessing novel properties for specific applications not exhibited by the particles of the same material at micro or macroscale. Nanostructures exist in various shapes and sizes commonly being the spheres, rods, wires and tubes (Cameotra and Dhanjal, 2010).

### 2.1.1 General properties of nanoparticles

In typical nanomaterials, a large fraction of the atoms are located on the surface of the particles, whereas in conventional materials, they are located in the bulk. As a result, many of the intrinsic properties of nanomaterials are different from conventional materials, since many of the atoms are in a different environment. Two key factors cause the properties of nanomaterials to differ significantly from other materials: increased surface area and quantum effects. Nanomaterials have much greater surface area per unit mass compared to conventional materials. As chemical reactions occur at surfaces, this means that a given mass of nanomaterials will be more accessible than the same mass of material made up of larger particles. In addition, higher surface energies and the presence of many corners, edges, and surface defects cause additional intrinsic reactivity. Quantum effects also begin to dictate the properties of matter as size is reduced to the nanoscale, which in turn affects the optical, electrical, and magnetic behavior of materials.

Since industrial sectors such as aerospace, biotech, energy, healthcare, and transportation depend on materials and devices made of atoms and molecules, they can all be improved by application of nanomaterials. Indeed, this rapidly advancing field of science has afforded a variety of commercially available products including catalysts, cosmetics, electronics, paints, self-cleaning windows, suntan lotions, and stainresistant clothing. All of the materials, the most commonly mentioned materials are carbon based on fullerenes and nanotubes, followed by silver, silica, titanium dioxide, zinc oxide, and cerium oxide. Iron nanoparticles appear to have potential for environmental applications, particularly for groundwater remediation. Nanoparticles of titanium dioxide and zinc oxide are included in personal care products such as toothpaste, beauty products, sunscreens, and textiles. Silver nanoparticles are used as antimicrobials in textiles such as socks and underwear and are recommended for use in food packaging and in detergents. Areas producing the greatest revenue for nanoparticles reportedly are chemical–mechanical polishing, magnetic recording tapes, sunscreens, automotive catalyst supports, biolabeling, electroconductive coatings, and optical fibers. The number of consumer products on the market containing nanomaterials (as particles or fibers) now exceeds 1,000 and is growing quickly. This count includes nanomaterials containing carbon, cerium oxide, silver, silica, titanium dioxide, magnesium oxide, and zinc oxide (Cameotra and Dhanjal, 2010).

### 2.1.2 Properties and applications of silver nanoparticles

Among various nanomaterials, silver nanoparticles are prominently used in many industries due to its excellent physiochemical properties (Ananth et al., 2014). In general, compared with sub-micro- and microparticles, nanoparticles have a large specific surface area and show characteristic physical and chemical properties such as high catalytic activity and broad absorbance spectrum. These characteristic properties are useful in industry and life science applications. Now, many kinds of nanoparticles are commercially produced and used as industrial products, for example, as sunscreens, cosmetics, and fuel additives. In addition, some nanoparticles are studied as novel functional materials, for example, in nanomedicine. Currently most of the applications of AgNP are in biotechnology, textile engineering and catalysis. The antimicrobial activity of silver ions has been documented by clinicians over several years. AgNPs possess unique physical and chemical properties due to their large surface area compared to volume, which provides better contact with microorganisms. Due to these improved properties, AgNPs get attached to the cell membrane and penetrate inside the microbial cell. The microbial cell contains electron donor groups like sulfur, oxygen, and nitrogen. Electrostatic interaction takes place between negatively charged electron donor groups and positively charged AgNPs, which brings structural and functional changes in the microbial cell membrane. Finally leading to cell death. The size, shape, and dispersity of AgNPs have also been shown to have immense impact on the antimicrobial efficacy of AgNPs. The nano size of the particles possesses a large surface area for contact with the microbial cell and hence exhibits better interaction than bigger particles. Regarding the shape of nanoparticles, truncated and triangular nanoparticles show better inhibition. Thus, among the different antimicrobial agents involved, silver as an antimicrobial agent possesses great potential and can be used efficiently in diverse applications ( Rai et al., 2012).

AgNPs have been used extensively as anti-bacterial agents in the health industry, food storage, textile coatings and a number of environmental applications. It is important to note that despite of decades of use, the evidence of toxicity of silver is still not clear. As anti-bacterial agents, AgNPs were applied in a wide range of applications from disinfecting medical devices and home appliances to water treatment. Moreover, this encouraged the textile industry to use AgNPs in different textile fabrics. In this direction, silver nanocomposite fibers were prepared containing silver nanoparticles incorporated inside the fabric. The cotton fibers containing AgNPs exhibited high anti-bacterial activity against Escherichia coli.

Furthermore, the electrochemical properties of AgNPs incorporated them in nanoscale sensors that can offer faster response times and lower detection limits. For instance, Manno et al. (2008) electrodeposited AgNPs onto alumina plates gold micro-patterned electrode that showed a high sensitivity to hydrogen peroxide.

Catalytic activities of nanoparticles differ from the chemical properties of the bulk materials. For instance, Kohler et al. showed that the bleaching of the organic dyes by application of potassium peroxodisulphate in aqueous solution at room temperature is enhanced strongly by the application of silver containing nanoparticles. Furthermore, AgNPs was found to catalyze the chemiluminescence from luminol–hydrogen peroxide system with catalytic activity beter than Au and Pt colloid.

The optical properties of a metallic nanoparticle depend mainly on its surface plasmon resonance, where the plasmon refers to the collective oscillation of the free electrons within the metallic nanoparticle. It is well known that the plasmon resonant peaks and line widths are sensitive to the size and shape of the nanoparticle, the metallic species and the surrounding medium (Abou El-Nour et al., 2010).

### 2.1.3 Effects of silver nanoparticles on microorganisms

Silver is the most widely used oligodynamic metal for water disinfection, due to its wide range of antimicrobial effect, low toxicity to humans, and ease of operation .The antimicrobial properties of silver have been known for centuries. Many examples of using silver to kill pathogens or prevent microbial growth can be found in history all overtheworld. To prevent water-borne diseases, people have used silver vessels to store water or have put silver coins in their barrels.

The antimicrobial properties of silver have been known for centuries. Many examples of using silver to kill pathogens or prevent microbial growth can be found in history all over the world. To prevent water-borne diseases, people have used silver vessels to store water or have put silver coins in their barrels (Russell et al., 1994).However, the exact mechanism which silver nanoparticles employ to cause antimicrobial effect is not clearly known and is a debated topic. There are however various theories on the action of silver nanoparticles on microbes to cause the microbicidal effect.The inhibitory mechanisms of nanosilver are mainly associatedwith the release of Ag ions from AgNPs (Miao et al., 2009; Navarro et al., 2008). The antimicrobial effect of silver ions has been published many time in the literature and may include the following mechanisms: (1) interact with thiol groups and inactivate critical enzymes; (2) interact with DNA and prevent DNA replication; (3) catalyze the generation of reactive oxygen species (ROS); (4) change the permeability of the cell membrane; and (5) interrupt the electron transport. Silver nanomaterials can disrupt the cell wall and penetrate through the cell membranes themselves, or they can kill the pathogens by releasing silver ions (Li et al., 2009). A schematic summarizing the possible mechanisms is shown in Figure 1. (Li et al., 2009). Smaller silver particles, less than 10 nm, are more toxic, because smaller particles are able to more easily penetrate the cell membranes. Furthermore, triangular silver nanoplates containing more {111} surface were found to be more toxic than nanorods, nanospheres, or silver ions (Lui et., 2012).

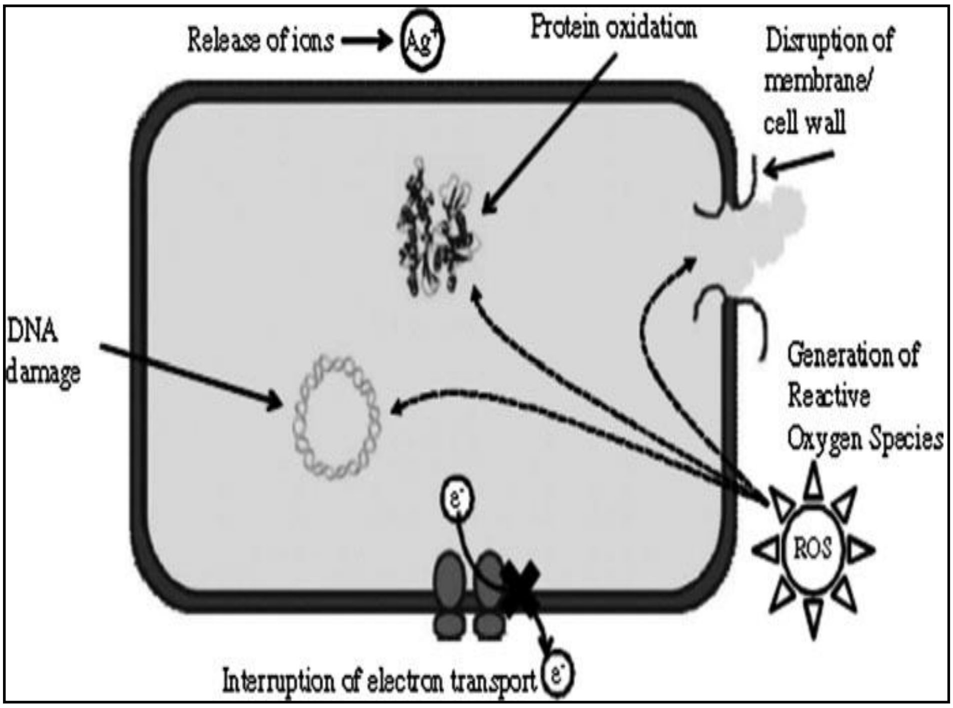



**Figure 2.1 :** A schematic of the possible mechanisms of antimicrobial activity of silver (Li et al., 2009).

### 2.2 Membrane Fouling

Membrane bioreactor (MBR) technology combines the biological degradation process by activated sludge with a direct solid–liquid separation by membrane filtration. By using micro or ultrafiltration membrane technology (with pore sizes ranging from 0.05 to 0. 4 μm), MBR systems allow the complete physical retention of bacterial flocs and virtually all suspended solids within the bioreactor. As a result, the MBR has many advantages over conventional wastewater treatment processes. These include small footprint and reactor requirements, high effluent quality, good disinfection capability, higher volumetric loading and less sludge production (Judd, 2006). However, membrane fouling is a major obstacle to the wide application of MBRs. Membrane fouling in MBRs can be attributed to both membrane pore clogging and sludge cake deposition on membranes which is usually the predominant fouling component (Lee et al., 2001). According to the pore size, Belfort et. al introduced three different fouling mechanisms (Figure 2): pore narrowing/constriction, pore plugging and gel/cake layer formation. In the case of pore narrowing, the foulant size (d) is much smaller than the pore size ($d_p$) and the foulants could adsorb into the pores, and could possibly close smaller pores. For the pore plugging, the foulant size (d) is at the same order of magnitude as the pore size (dp) and the foulants could plug the pores in the absence of adsorption. For the cake layer formation, the foulant size (d) is much bigger than the pore size (dp) and the foulants are not able to enters the pores thereby particles deposit on the surface of membrane to form a loose gel or a cake layer (Chaharmahali, 2012).

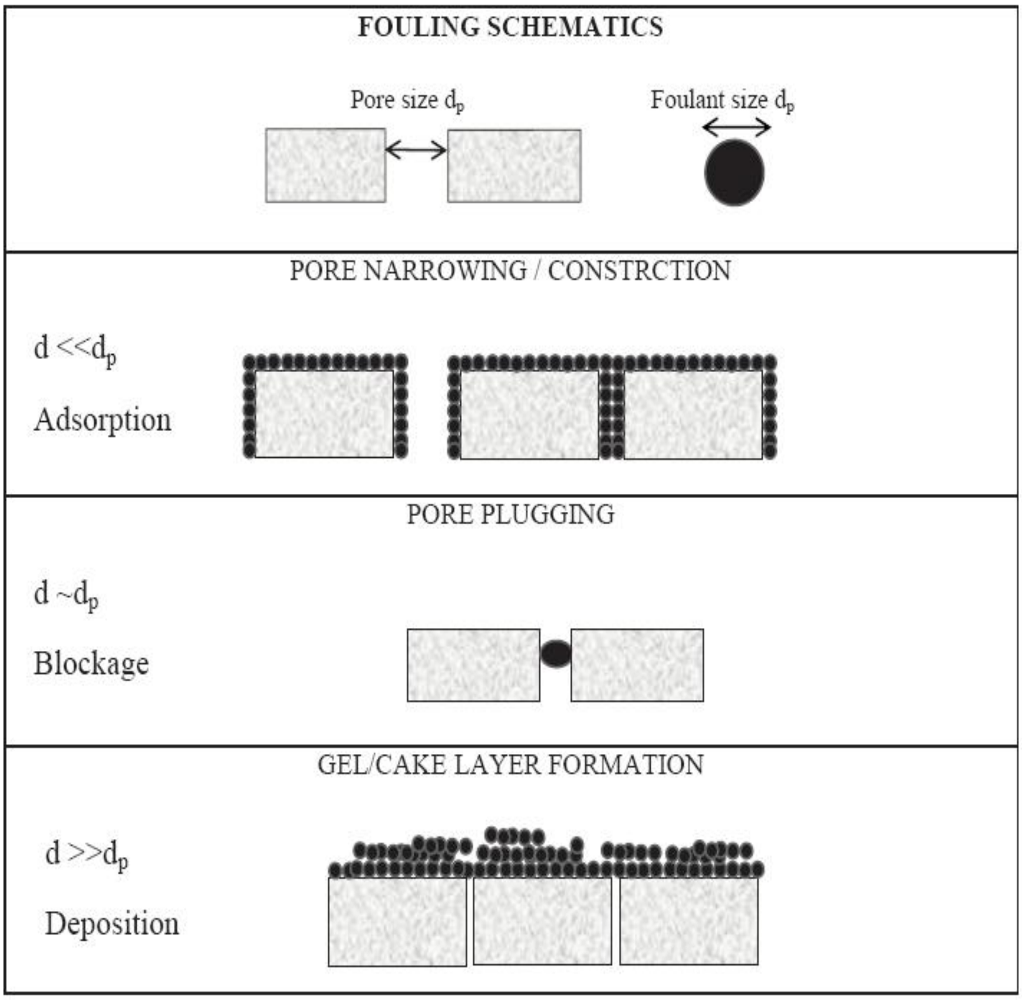



**Figure 2.2 :** Fouling schematics of pore narrowing or constriction, pore plugging and gel or cake layer formation

### 2.2.1 Classification of membrane fouling

#### 2.2.1.1 Removable and irremovable fouling

Membrane fouling is a very complicated phenomenon and results from multiple causes. Particle sizes of sludge flocs, colloids and solutes in mixed liquor may strongly affect fouling mechanisms in a membrane filtration system. If foulants are comparable with the membrane pores (i.e., colloids), or smaller than the membrane pores (i.e., solutes), adsorption on pore wall and pore blocking may occur. However, if foulants (i.e., sludge flocs and colloids) are much larger than the membrane pores, they tend to form a cake layer on the membrane surface.The removable fouling can be easily eliminated by implementation of physical cleaning (e.g., backwashing) while the irremovable fouling needs chemical cleaning to be eliminated. The removable fouling and reversible fouling are the same. The removable fouling is caused by loosely attached foulants; however, irremovable fouling is caused by pore blocking and strongly attached foulants during filtration. The irreversible fouling is a permanent fouling which can not be removed by any approaches (Meng et al., 2009).

#### 2.2.1.2 Biofouling, organic fouling and inorganic fouling

**Biofouling**

From the viewpoint of fouling components, the fouling in MBRs can be classified into three major categories: biofouling, organic fouling, and inorganic fouling.A fundamental understanding of the formation of membrane foulants will help us to propose more effective approaches for fouling control. Biofouling refers to the deposition, growth and metabolism of bacteria cells or flocs on the membranes, which has aroused a significant concern in membrane filtration processes. For a low pressure membrane such as microfiltration and ultrafiltration for treating wastewater, biofouling is a major problem because most foulants (microbial flocs) in MBRs are much larger than the membrane pore size. Biofouling may start with the deposition of individual cell or cell cluster on the membrane surface, after which the cells multiply and form a biocake. Many researchers suggest that SMP and EPS secreted by bacteria also play important roles in the formation of biological foulants and cake layer on membrane surfaces (Meng et al., 2009).

**Organic fouling**

Organic fouling in MBRs refers to the deposition of biopolymers (i.e., proteins and polysaccharides) on the membranes. Due to the small size, the biopolymers can be deposited onto the membranes more readily due to the permeate flow, but they have lower back transport velocity due to lift forces in comparison to large particles (e.g., colloids and sludge flocs). Recently, in order to provide a unique insight into the composition (protein and carbohydrate), have performed a more detailed study to characterise deposited biopolymers in MBRs. After membrane filtration, the fouling layers were fractionated into upper layer, intermediate layer and lower layer by using rinsing, backwashing and chemical cleaning. The results showed that the upper fouling layer was composed of a porous, loosely bound cake layer with a similar composition to the sludge flocs. The intermediate fouling layer was contributed equally by SMP and bacteria aggregates, and had a high concentration of polysaccharides. The lower layer, representing the irremovable fouling fraction and predominated by SMP, had a relative higher concentration of bound proteins (Meng et al., 2009).

**Inorganic fouling**

In general, membrane fouling in MBRs is mainly governed by biofouling and organic foulingrather than by inorganic fouling, although all of them take place simultaneously during membrane filtration of activated sludge. Up to now, thereby, most of the researchers attributed membrane fouling to the deposition of bacteria cells and biopolymers; the inorganic fouling in MBRs has been mentioned by only a few papers.Ognier et al. (2002) pointed out there was severe $CaCO_3$ fouling in a pilot MBR with a ceramic ultrafiltration membrane module. In this study, the synthetic wastewater was prepared with hard tap water (concentrations of $Ca^{+2}$ and $Mg^{+2}$ are 120 mg/L and 8 mg/L, respectively). They found that the high alkalinity of the activated sludge (pH= 8–9) could cause the precipitation of $CaCO_3$. The investigations by Kang et al. (2002) and Ognier et al. (2002) suggested that on inorganic membranes inorganic fouling may ocur more easily. In general, a cake of inorganic matter can be irremovable due to the cohesive properties. More recently, Wang et al. (2008b) observed that the cake layer was formed by organic substances and inorganic elements such as Mg, Al, Fe, Ca, Si, etc. The organic foulants coupled with the inorganic precipitation enhance the formation of a cake layer. Lyko et al. (2007) also found that metal substance was a more significant contributor to membrane fouling than biopolymers. Sometimes, the fouling caused by inorganic scaling is not easy to be eliminated even by chemical cleaning. These findings indicate that inorganic fouling has become more and more important in MBRs. But, the understanding of inorganic fouling is still not clear. The investigation on the limiting concentration of metal ions in the feed wastewater that can lead to inorganic fouling will be of great interest, since the chemical composition of the wastewater is in close relation with the formation of precipitation (Meng et al., 2009).

## 2.4 Membrane Fouling Affecting Factors

The factors affecting membrane fouling can be classified into four groups: membrane materials, biomass characteristics, feedwater characteristics, and operating conditions. The complex interactions between these aspects complicate the understanding of membrane fouling. For a given MBR process, the fouling behaviour is directly determined by sludge characteristics and hydrodynamic conditions. But, operating conditions (i.e., SRT, HRT and F/M) and feedwater have indirect actions on membrane fouling by modifying sludge characteristics (Meng et al., 2009).

### 2.4.1 Bound EPS and SMP

EPS in either bound or soluble form are currently considered as the predominant cause of membrane fouling in MBRs. Bound EPS consist of proteins, polysaccharides, nucleic acids, lipids, humic acids, etc. which are located at or outside the cell surface. Soluble EPS and SMP are the same. SMP can be defined as the pool of organic compounds that are released into solution from substrate metabolism (usually with biomass growth) and biomass decay (Barker and Stuckey, 1999). Thus, SMP can be subdivided into two categories: substrate-utilisation-associatedproducts (UAP), which are produced directly during substratemetabolism, and biomass-associated products (BAP), which areformed from biomass, presumably as part of decay.The interrelations between bound EPS and SMP are verycomplex. A unified theory for EPS and SMP was proposed byLaspidou and Rittmann (2002), who pointed out that cells useelectrons from the electron-donor substrate to build activebiomass, and they produce bound EPS and UAP in the process.Part of the bound EPS can be hydrolysed to BAP. Some SMP canbe utilised by active biomass as recycled electron donors; andsome can be adsorbed by the biomass flocs and then, becomebound EPS. In addition, the generation of bound EPS and UAPis in proportion to substrate utilisation (Meng et al., 2009).

#### 2.4.1.1 Bound EPS

Bound EPS have been reported not only as major sludge floc components keeping the floc in a three-dimensional matrix, but also as key membrane foulants in MBR systems. Cho et al.(2005) found a close relationship between the bound EPS and the specific cake resistance and established a functional equation in which the specific cake resistance was proportional to the EPS concentration. Ahmed et al. (2007) also observed that as bound EPS concentration rose, the specific cake resistance increased, and this consequently resulted in the rise of the transmembrane pressure ( TMP). Several studies, however, reported that bound EPS had little correlation with membrane fouling. Rosenberger and Kraume (2003) found that contrary to some literature, no impact of bound EPS on the filterability could be observed. Instead, the soluble EPS or SMP was found to have great impact on the filterability of sludge. This was confirmed by a more recent work reporting no clear relation between bound EPS and membrane fouling as its concentration was smaller than 10 mg/g SS. In order to have a beter understanding of sludge characteristics and their effects on membrane fouling, several investigations have been carried out. These investigations showed that activated sludge has very complex impacts on membrane fouling process. Bound EPS cannot be considered as the sole cause for membrane fouling, even though it has great effects on sludge characteristics and membrane fouling Therefore, considering the important roles of bound EPS in sludge characteristics and membrane fouling, bound EPS should be controlled in order to mitigate membrane fouling more efficiently (Meng et al., 2009).

#### 2.4.1.2 SMP

In fact, fouling behaviour cannot be attributed solely to bound EPS due to the complex nature of sludge suspension. Recently, the influence of SMP on MBR fouling has attracted much attention. Due to the membrane rejection, the SMP is more easily accumulated in MBRs, which results in the poor filterability of the sludge suspension. Geng and Hall (2007) observed that the floc size distribution and the amount of soluble EPS or SMP in the mixed liquor were the most important properties that significantly influenced the fouling propensity of sludge, but the content of bound EPS was not found to be directly associated with membrane fouling. Since SMP has been recognized as significant membrane foulant,scientific research on SMP or sludge supernatant becameone of the hot topics in membrane fouling. These investigations suggest that the occurrence of SMP in MBRs impacts on  membrane fouling significantly, and SMP concentration and SMP composition would determine its fouling propensity (Meng et al., 2009).

### 2.4.2. Membrane material properties

Membrane characteristics such as pore size, porosity, surface charge, roughness, and hydrophilicity/hydrophobicity, etc., have been proven to impact on MBR performance, especially on membrane fouling. The determination of suitable membrane pore sizes has been extensively investigated in the 1990s. Pore size distribution is likely to be one of the parameters affecting membrane performance. A narrow pore size distribution is preferred to control membrane fouling both in MBR process and in conventional membrane separation process. The membrane materials always show different fouling propensity due to their different pore size, morphology and hydrophobicity. In general, membrane fouling occurs more readily on hydrophobic membranes than on hydrophilic ones because of the hydrophobic interaction between foulants and membranes. As a result, much attention has been given to reduce membrane fouling by modifying hydrophobic membranes to relatively hydrophilic (Meng et al., 2009).

### 2.4.3 Fouling control strategies with nanocomposite membranes

The reliability and ease of operation of membrane-based water filtration systems have led to their increasing use in water and wastewater treatment. However, biofouling of these membranes, including microbial release of extracellular polymeric substances (EPS), and the associated decrease in membrane flux, increases energy costs and shortens membrane life. Certain membrane characteristics affect the likelihood of biofouling, including surface charge and hydrophobicity, and membrane biofouling is commonly controlled with pretreatment (coagulation) or with chemical cleaning (e.g., chlorine) during backwash. Although pretreatment can be an effective form of biofouling control, many polymeric membranes can not withstand the corrosiveness of chemical cleaners. Biofouling is counteracted by using the bactericidal properties of nanoparticles, of which silver is the most commonly used bactericide for fouling reduction. Silver impregnated membranes were proven to be effective against two strains of bacteria, *E. coli* K12 and *P. mendocina* KR1 that were both found in wastewater . In recent years many reports showed the importance of AgNPs in dictating the required membrane properties for water industries such as porosity, mechanical strength and anti-microbial effects. These membranes not only had antimicrobial properties, but they also prevented bacterial attachment to the membrane surface and thus reduced biofilm formation(Zodrow et al., 2009).

Membrane surface chemistry plays an important role to enhance the separation performance. One of the properties that may influence membrane surface performance is membrane hydrophilicity/hydrophobicity (Basri et al., 2011). More severe fouling is expected when hydrophobic membranes are used in the MBR, and efforts have been focused on increasing membrane hydrophilicity through membrane modification (Le-Clech et al., 2006).Achievement of an improved water permeability, hydrophilicity and reduced fouling are the main focus of interest in membrane separation processes. To ensure that, properties such as mechanical, thermal, surface and internal structures, chemical and bio-stability of the membranes have to be engineered carefully. The surface chemical activity rendered by nanomaterials is a desired phenomenon and being exploited for a variety of applications especially in water decontamination, catalysis and related environmental remediation applications (Ananth et al., 2014).

### 2.5 Usage of suspended Ag nanoparticles on wastewater treatmentperformance

Nanoscience and nanotechnology are dynamically developing fields of scientific interests in the entire world. This technology promises scientific advancements in various sectors such as medicine, consumer products, energy, materials and manufacturing. Nanotechnology is somewhat loosely defined, although in general terms it covers engineered structures, devices, and systems that have a length scale between 1 and 100 nanometers. Researching, developing and utilizing are the heart of this new technology. Nanotechnology offers potentially huge benefits to society, industry, environment and health. It helps us to improve quality of our lives and responds some key issues of day as climate change by reducing greenhouse gas emissions. Other potential benefits include contributions in improving energy storage and efficiency, better diagnosis and treatment of disease, faster computer systems and remediation of air, soil or water pollution.Rapid expansion of the nanotechnology industry has occurred over the previous decade. Manufactured nanomaterials (MNMs) encompass a variety of engineered materials, which can be divided into two groups for the sake of clarity: nano-sized particles (having at least two dimensions < 100 nm) and secondly, materials that are not particulate but have nano-sized properties (i.e. enhanced electronic, optical and chemical properties compared to the bulk material). Silver nanoparticles are the most widely used NPs in both consumer products and in medical applications. The anti-bacterial properties that render AgNPs desirable may lead to increased risks to human and environmental health following release into the environment. The primary exposure pathway of AgNPs into the environment is via wastewater streams. Silver NPs may enter wastewater through the washing of Ag nano-containing textiles or plastics or as a result of the use of nano-enhanced outdoor paints and washing machines. Several authors have investigated the fate of manufactured AgNPs in wastewater treatment plants (WWTPs) and have reported that the majority (> 85%) of AgNPs will be captured by biosolids (stabilised sludge). Accordingly, the predicted effluent concentrations of AgNP are very low (μg $L^{-1}$), whereas AgNP concentrations in sludge are predicted to be much higher (1 – 6 mg Ag $kg^{-}$

$^{1}$) . Both concentrations are likely to increase as the AgNP producing industry expands. Given this scenario, and the strong anti-bacterial effects of AgNPs, the stages of WWT that are likely to be affected by AgNPs are those that are dependent on the efficient functioning of microbes. Such stages are the aerobic activated sludge process and anaerobic digestion, which proceeds the former process in most WWTPs. There are very few studies that have investigated the impact of AgNPs on both processes in a sequential manner. Given that the transformation of AgNPs is likely during WWT, it is crucial to understand at what stage transformation occurs so accurate risk assesments can be conducted using AgNPs in realistic forms. During the activated sludge process,organic nitrogen and phosphorus are removed by various microbial communities. Several studies have investigated the impact of AgNPs on nitrification and the effects on microbial populations that perform these processes. However, results from nitrification studies are divergent with no inhibition and varying degrees of inhibition observed on nitrification following AgNP addition in WWTPs or bioreactors at concentrations between 0.4 and 1 mg Ag $L^{-1}$. The observed variation is most likely explained by the differences in input variables. A number of parameters differ between studies, all of which are known to influence AgNP fate and toxicity e.g. intrinsic AgNP properties (size, coating), Ag concentration, sludge/wastewater properties (temperature, ionic strength (IS)), total suspended solids (TSS) and dissolved organic carbon, (DOC)), the type of sludge/wastewater used (realistic or artificial) and general experimental set-up (e.g. light intensity and wavelength which may cause photocatalytic reduction of Ag+ and AgNP).

The bactericidal mechanism of AgNPs (and $Ag^{+}$ ) to organisms is only partially understood and debate is ongoing as to the exact means of action. However, there is concern that the same properties that render AgNPs useful as an antimicrobial may also impact WWTP performance by affecting sludge microbial populations. A high diversity of bacterial populations in WWTPs is crucial for successful removal of BOD/COD, SS and biological phosphorus and nitrogen. The effects of AgNPs on sludge microbial communities have been investigated by a limited number of studies. The model nitrifying bacteria Nitrosomonas europae has been shown to be adversely affected by AgNPs at concentrations of 0.3 mg Ag $L^{-1}$ and 2 mg Ag $L^{-1}$. These are much higher Ag concentrations than would normally be found in the environment at present (Doolette et al., 2013).

## 3. EXPERIMENTAL METHOD

### 3.1 Materials

Silver ($Ag^0$, <100 nm) nanoparticle was purchased from NanoAmor (Texas, USA). The photograph of the nanomaterial are shown in Figure 3.1. For preparation of synthetic domestic wastewater, glucose, urea, $(NH_4)_2SO_4$, $NaHCO_3$, $MgSO_4$, $KH_2PO_4$ (Merck), $K_2HPO_4$ and formaldehyde (37%), NaOH used for biological substances analysis were purchased from Merck. Also, folin, $Na_2CO_3$, $Na_2$tartarate.$2H_2O$, BSA and $CuSO_4.5H_2O$ for protein analysis and phenol and $H_2SO_4$ (%95-97) for carbohydrate analysis were purchased from Merck. Also, brands and product codes of solvent, polymer and the nanomaterial are indicated in Table 3.1. Chemicals are used without extra purification.

**Table 3.1 :** Brands and product codes of materials used for the experiment.

| **Chemical Name** | **Brand** | **Code** |
|---|---|---|
| Polyethersulfon (PES, Mw=10000 Da) | BASF | UltrasonE6020P |
| Polyvinylpyrrolidone (PVP, Mw=10000 Da) | Sigma-Aldrich | PVP10 |
| 1-Methyl-2-pyrrolidinone (NMP) | Sigma-Aldrich | 328634 |
| Silver nanoparticles (Ag) | NanoAmor | 0476JY |


**Figure 3.1 :**Nanomaterial, AgNP used for producing the nanocomposite membrane.

## 3.2 Characteristic of Membranes

Experiments were carrid out with bare PES membrane and AgNP-PES composite membrane produced in the National Membrane Technologies Research Center (MEMTEK). Polymer, PVP and solvent ratio of bare PES membrane is 14, 8 and 78 (% weight), respectively. Silver nanoparticle, polymer, PVP and solvent ratios of AgNP-PES composite membrane is 1,2, 14, 8 and 78 (% weight), respectively.

## 3.3 Analytical Methods

### 3.3.1 Mixed liquor suspended solids (MLSS)

Before feeding the aerated activated sludge, 5 mL activated sludge sample was taken from the experimental medium on daily basis. A filter was taken from a dessicator and its tare was weighted ($m_1$). Activated sludge sample was filtered from MLSS set under vacuum conditions. The filter was dried in oven at 105°C for one hour. Upon drying, the filter was waited in the desiccator for 1 h, and then the filter was weighed ($m_2$). MLSS is calculated by following equation;

$$AKM\ \left(\frac{mg}{L}\right) = \frac{(m_2 - m_1)}{ml\ numune\ hacmi} x1000$$

### 3.3.2 Filtration system

Sterlitech HP4750 branded magnetic stirrer containing classical filtration cell was used for the filtration experiments. Pressure in the device was adjusted by using nitrogen gas while the cross flow on the membrane surface was provided by stirring. Properties of the filtration system are indicated in the Table 3.2as stated by the producer company.

**Table 3.2 :** Technical properties of the filtration system.

| **Parameter** | **Value** |
|---|---|
| Membrane diameter | 49 mm |
| Active membrane area | 14.6 $cm^2$ |
| Volume | 300 ml |
| Maximum pressure | 69 bar |
| Maximum temperature | $121^0$C |

Preparation steps of the filtration process are shown in the Figure 3.2. Experiments in the filtration cell are explained below in details.

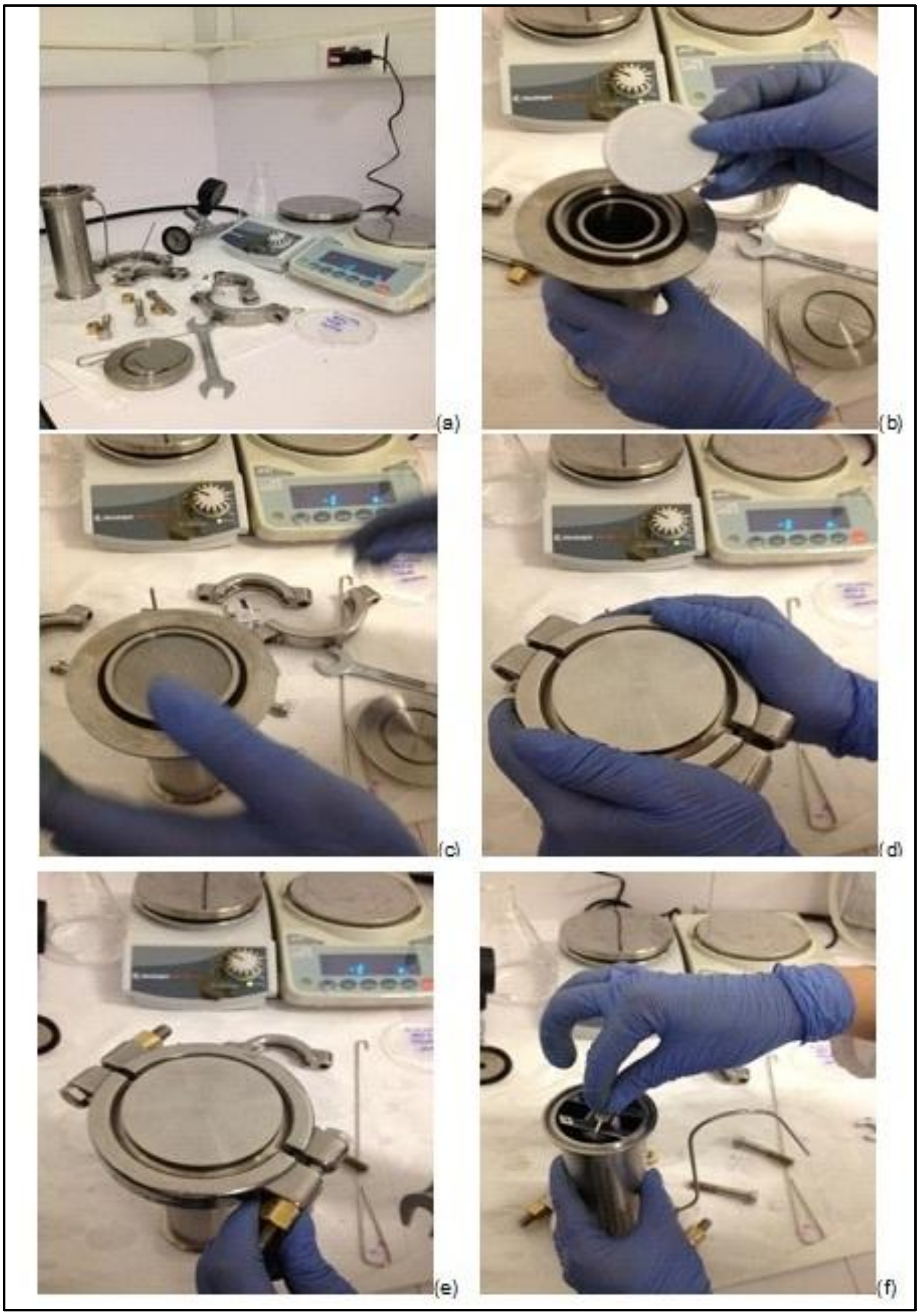


**Figure 3.2 :**Preparation of the filtration cell.

### 3.3.3 Biological substances analysis (extracellular polymeric substances-EPS)

Extracellular polymeric substances (EPS) are the construction materials for microbial aggregates such as biofilms, flocs and activated sludge liquors. The term "EPS" is used as a general and comprehensive concept for different classes of macromolecules such as polysaccharides, proteins, nucleic acids, (phosphor-)lipids and other polymeric compounds which have been found at or outside the cell surface and in the intercellular space of microbial aggregates. They consist of insoluble materials (sheaths, capsular polymers, condensed gel, loosely bound polymers and attached organic material) produced by active secretion, shedding of cell surface material or cell lysis. The term "EPS" is used as a general parameter to characterize bio-polymeric substances in the reactor. It is important to recognize that the exact definitions of eEPS (extracted extracellular polymeric substances), and sEPS (soluble extracellular polymeric substances) are directly dependent of the methods used to obtain and characterize chemically these solutions. In literature, it has been now widely accepted that the concepts of sEPS and soluble microbial products (SMP) are identical. Also only EPS term was generally used for eEPS parameter (Le-Clech, et. al., 2006). The usage of EPS terms is given at Figure 3. 3.

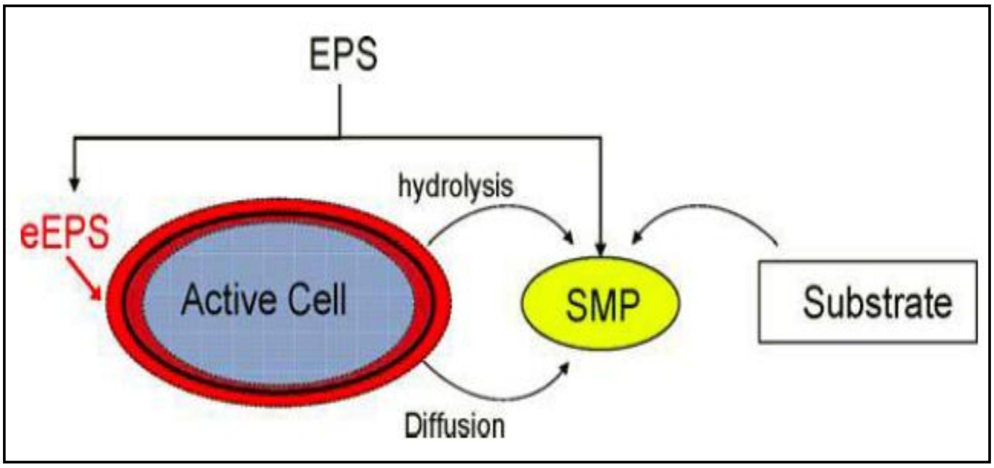
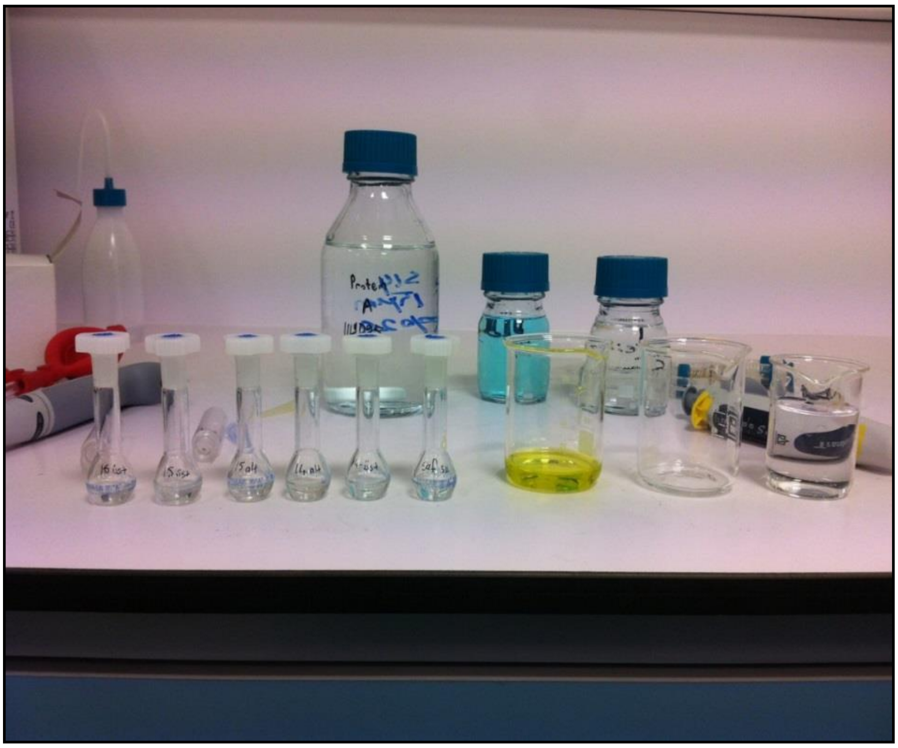



**Figure 3.3 :** Simplified representation of EPS, eEPS and SMP (Le-Clech, et. al., 2006).

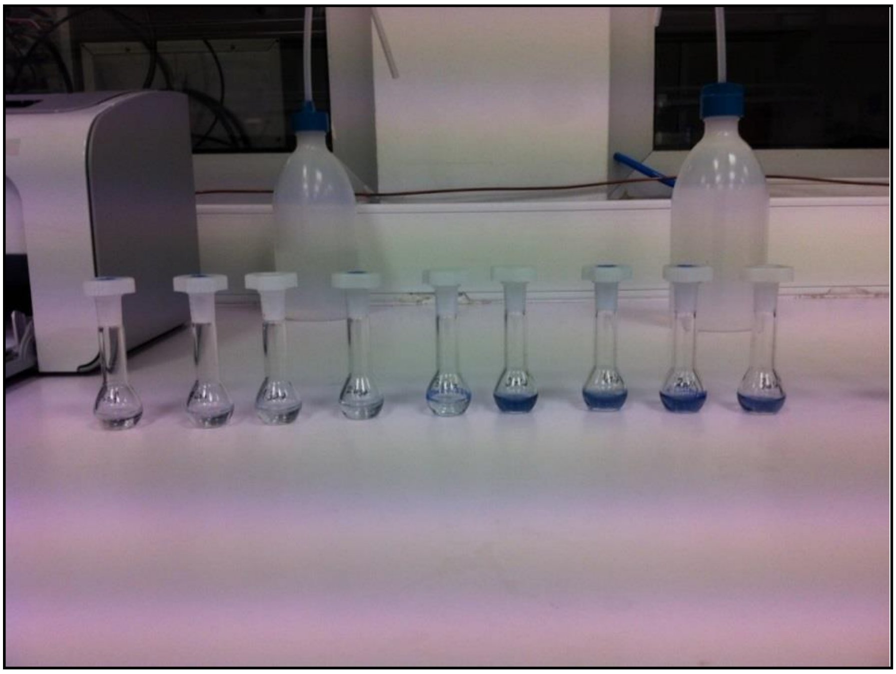
In this study, SMP and EPS analysis were carried out on daily samples of activated sludge. For those analysis, physical-chemical (sodium hydroxide – formaldehide) extraction method was used. Formaldehide prevents cellular decomposition by reacting with nucleic acids, and amino, hidroxile, carboxil and sulfide groups of proteins in cell membrane. Consequently, cellular forms are protected. NaOH increases the pH, and the pH of the solution of EPS is increased, hence, more EPS is extracted from the cell. 5 ml of activated sludge from each experimental vessel was taken into a centrifuged tube and then the suspension was centrifuged (4000×g, 10min, 40C). The supernatant was decanted into another sterile tube and recentrifuged (13.200×g, 20min, 40C) to ensure complete removal of the suspended solids. The resultant supernatant by this physical extraction contained soluble carbohydrate and soluble protein, and was analyzed for soluble EPS content (SMP). The solid flocs in the tube were resuspended with distilled water to obtain another 5ml suspension. Then, 6 µL formaldehyde (37%) was added first into the suspension for 1 h at 4 ◦C, followed by 0.5 ml NaOH (1N) for another 3 h at 4 ◦C. The suspension was centrifuged (13.200×g, 20min, 4 ◦C) and the supernatant from this chemical extracting method, containing bound carbohydrate and bound protein, was analyzed for bound EPS content. Carbohydrate concentrations were quantified by the phenol–sulfuric acid method. Protein concentrations were determined by using the modified Lowry method. Carbohydrate and protein analysis methods are given in following sections.

### 3.3.4 Protein analysis method

The real-time photographs of protein analysis in the experimental system are given at Figure 3.4.Three main solutions (A,B and C solutions) were prepared for analysis of Lowry protein method. 2.86 g NaOH and 14.31 g $Na_2CO_3$ were dissolved in distilled water and diluted to 500 ml for preparation of the solution A. 1.42 g $CuSO_4.5H_2O$ was dissolved in 100 ml distilled water for preparation of the solution B. And, 2.85g $Na_2$tartarate.$2H_2O$ was dissolved in 100 ml distilled water for preparation of the solution C. Lowry solution was prepared by mixing these three solutions with a specific rate of 100:1:1 (A:B:C) right before the analysis. 0.7 ml Lowry solution was added to 0.5 ml sample and stirred for 20 min at room temperature in a dark place. Folin solution was prepared during this stage. Then, 5 ml of 2N Folin solution was mixed with 6 ml of distilled water. 0.1 ml of folin solution was mixed with 0.5 ml of the sample and kept in a dark place for 30 min after vigorous stirring. Afterwards, samples were colored from light to dark blue according to their protein concentrations. Measurements were done by using a UV spectrophotometer, obtained from Hach Lange Company, at a constant wavelength (660 nm). Reference solution was also prepared under the same conditions for the measurements. Two similar solutions were prepared and measured for each solution in order to provide repeatability for the measurements.



(a)



(b)

**Figure 3. 4 :** The photographs of protein analysis experimental systems.

Bovin Serum Albumin (BSA) was used as the standard protein solution for protein calibration. Solutions having concentrations in the range of 0-100 mg/L were prepared by using the standard protein. Absorption values were measured at 660 nm by using a UV spectrophotometer. The absorption-concentration graph was drawn with the obtained values. Calibration graph is given in the Figure 3. 5.

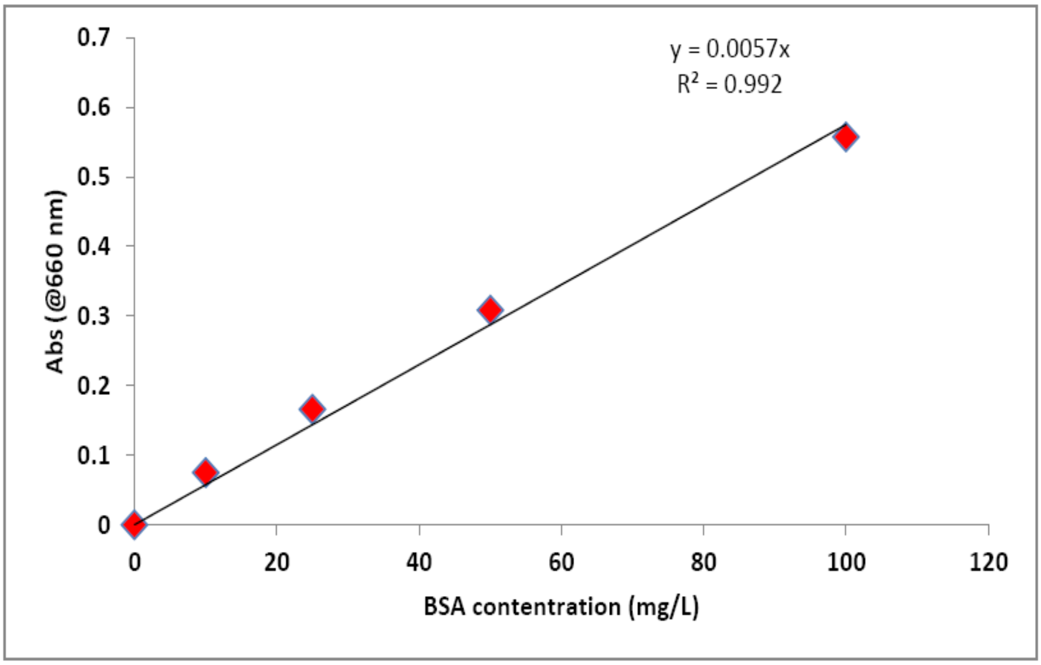



**Figure 3.5 :**Calibration curve for protein analysis.

### 3.3.5 Carbohydrate analysis method

Modified "phenol-sulfuric acid method" was used for the carbohydrate analysis. Among many colorimetric methods for carbohydrate analysis, the phenol-sulfuric acid method is the easiest and most reliable method. It has been used for measuring neutral sugars in oligosaccharides, proteoglycans, glycoproteins, and glycolipids. This method is used widely because of its sensitivity and simplicity.

Phenol solution with concentration of 80% and concentrated $H_2SO_4$ (95-97%) were used for the analysis. 25 µL of phenol and 2.5 mL of $H_2SO_4$ were added to 1 ml of sample at 300C and kept in a water bath for 15 min. Colors of the samples were varied from light yellow to dark yellow according to their carbohydrate concentrations. Colors were investigated by using a UV spectrophotometer at 490 nm wave length. The photograph of carbohydrate analysis is given at Figure 3.6. Glucose was used as the standard for calibration. Solutions having concentrations in the range of 2-80 mg/L were prepared by using the standard glucose. Calibration curve is shown in the Figure 3.7.

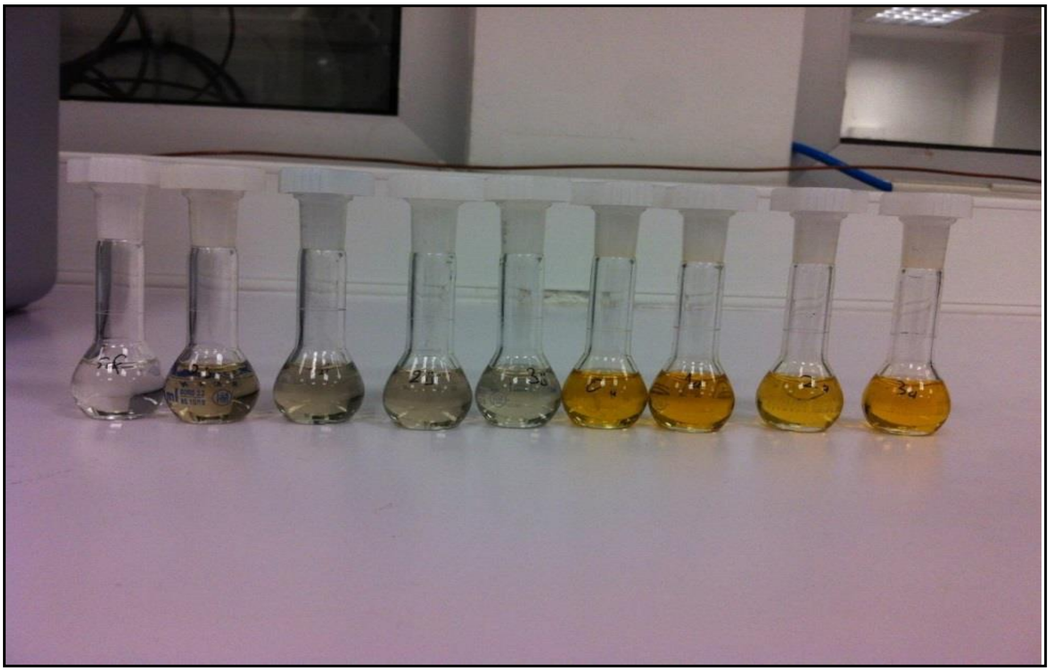


**Figure 3.6 :** The photograph of carbohydrate analysis experimental systems

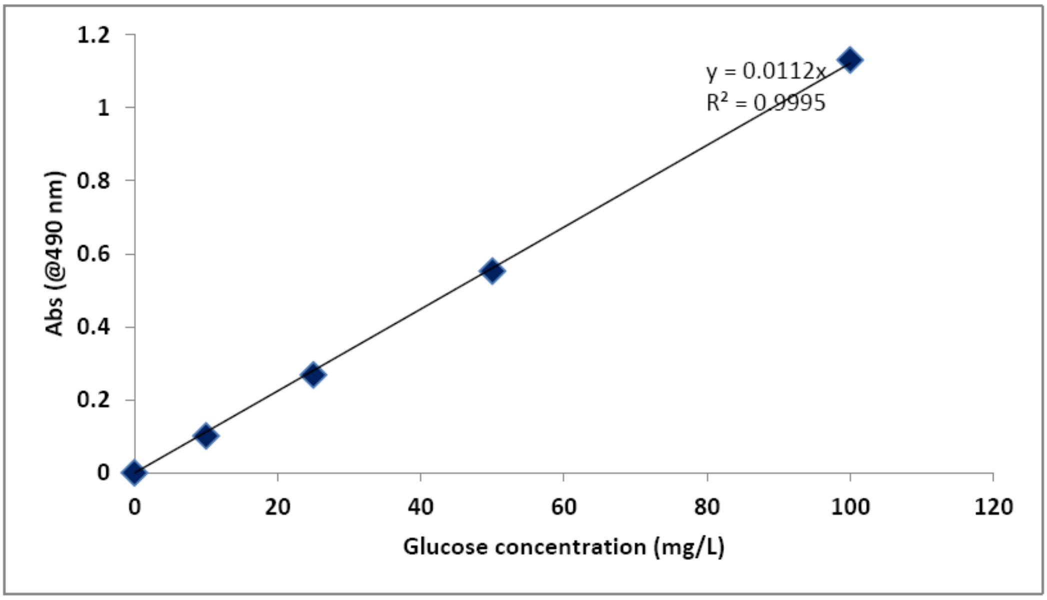



**Figure 3.7 :**Calibration curve for carbohydrate analysis.

### 3.3.6 Optical density

During long term analysis, in order to observe the bacterial growth and the setttling properties at activated sludge, the optical density measurement was carried out both at activated sludge and at supernatant of activated sludge, at permeate after settling time of 30 min. For this analysis, 3 ml of samples were taken from activated sludge, supernatant and permeate suspensions. Then, OD (optical density) values were scanned in Hach-Lange DB5000 spectroscopy device at a wavelength of 600 nm. OD values measured at activated sludge, supernatant, permeate were named as $OD_{sludge}$, $OD_{supernatant}$ and $OD_{permeate}$.

### 3.3.7 COD analysis

In order to analyze wastewater treatment performance, COD analyses was done with closed-reflux method as defined in Standart Methods. Sample of COD was taken from the permeate. Firstly, 1.5 ml potasyum dikromat and 3,5 ml sulfiric acid were put in test tube. After this, permeate sample of 2.5 ml was added on dikromat and acid mixture. Prepared COD sample was boiled in heat block for 2 hours at $150^0$C. After this process, test tube was left to cooling at room temperature. Sample dropped ferroin indicator was titrated with 0.025 N FAS (ferrous amonyum sulfate). Experiments of COD was carried out with blank sample by using distilled water. COD content of sample was calculated as folows:

$$COD\left(\frac{mg}{L}\right) = \frac{(A-B)x0.025x8000}{2.5}$$

A: FAS consumption volume for blank titration (ml)

B: FAS consumption volume for sample titration (ml)

### 3.3.8 TKN and TP Analyses

TP values were measured with Hach-Lange standart kits (Kit number:LCK 350).TKN analysis was done using Kjeldahl digestion method.

## 3.4 Experimental Setup

### 3.4.1 Preparation of Silver Stock Solution

In order to use at the experiments, the stock solution containing 10 mg AgNP/L was prepared. The preparation of stock solution is that 0.01 gr AgNP was dissolved in 200 ml distilled water by using sonication probe for 35 minutes. After that, this solution was completed to 1000 ml and it was continued to dissolve by stirring for 2 days. The photograph of dissolution of AgNP by using sonication probe is given at Figure 3.8.


**Figure 3.8 :**Dissolution of AgNP by using sonication probe.

### 3.4.2 Short-Term suspended silver nanoparticle exposure

The effects of suspended AgNP exposure on filtration performance and bacterial products were firstly carried out with short-term experiments. To begin with, in the first stage of these experiments, seven different exposure times (2, 4, 6, 17, 20, 24 and 48 hours) were studied, while suspended AgNP concentration was constant as 10 mg/L. After this, in the second stage of these experiments, the best suitable exposure times were selected and the short-term experiments were carried out in the three different suspended AgNP concentration (5, 2,5, 1 mg/L) while exposure time was constant. Activated sludge samples were freshly taken from a MBR system operated in the laboratories of National Membrane Technologies Research Center (MEMTEK). For the preparation of the experimental setup, 10 ml stock solution containing 10 mg AgNP/L and 40 ml activated sludge were mixed in a erlenmeyer flask and air stone was thrown into erlenmeyer flask then the experiments were launched. Also, control system was set up by using activated sludge without AgNP. The photograph of the experimental setup is given at Figure 3.10. In the end of exposure times, mixtures in the erlenmeyer flask were used for determining filtration performance of bare PES membrane. For this, Sterlitech HP4750 branded magnetic stirrer containing classical filtration cell was used and the effects of exposure times on filtration performances were determined based on fluxes for every exposure time. Besides, in the end of exposure times, mixtures in the erlenmeyer flask were analyzed for determining its protein and carbohydrate contents. For this, EPS and SMP analyses were carried out and the effects of exposure times on bacterial products were determined.After determining the effects of exposure times on filtration performance and bacterial products, as mentioned at the beginning, the best appropriate exposure times which are  6 and 17 hours were selected and in this stage, experiments were carried out in three different concentions (5, 2.5, 1 mg/L) while exposure time was constant. These mentioned concentrations were derived from stock solution containing 10 mg AgNP/L by diluting. Similarly, in the end of exposure times, mixtures were analyzed in terms of filtration performance and protein and carbohydrate contents. Consequently, the effects of short-term suspended AgNP exposure at different concentration on filtration performance and bacterial products were determined. First and second stage carried experiments of short-term exposure is summarized in Figure 39.

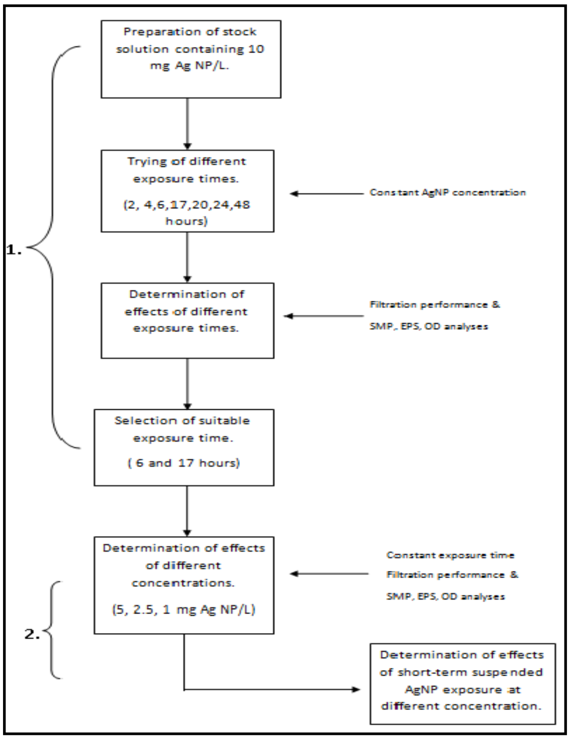



**Figure 3.9 :**The shematic diagram of short-term carried experiments.

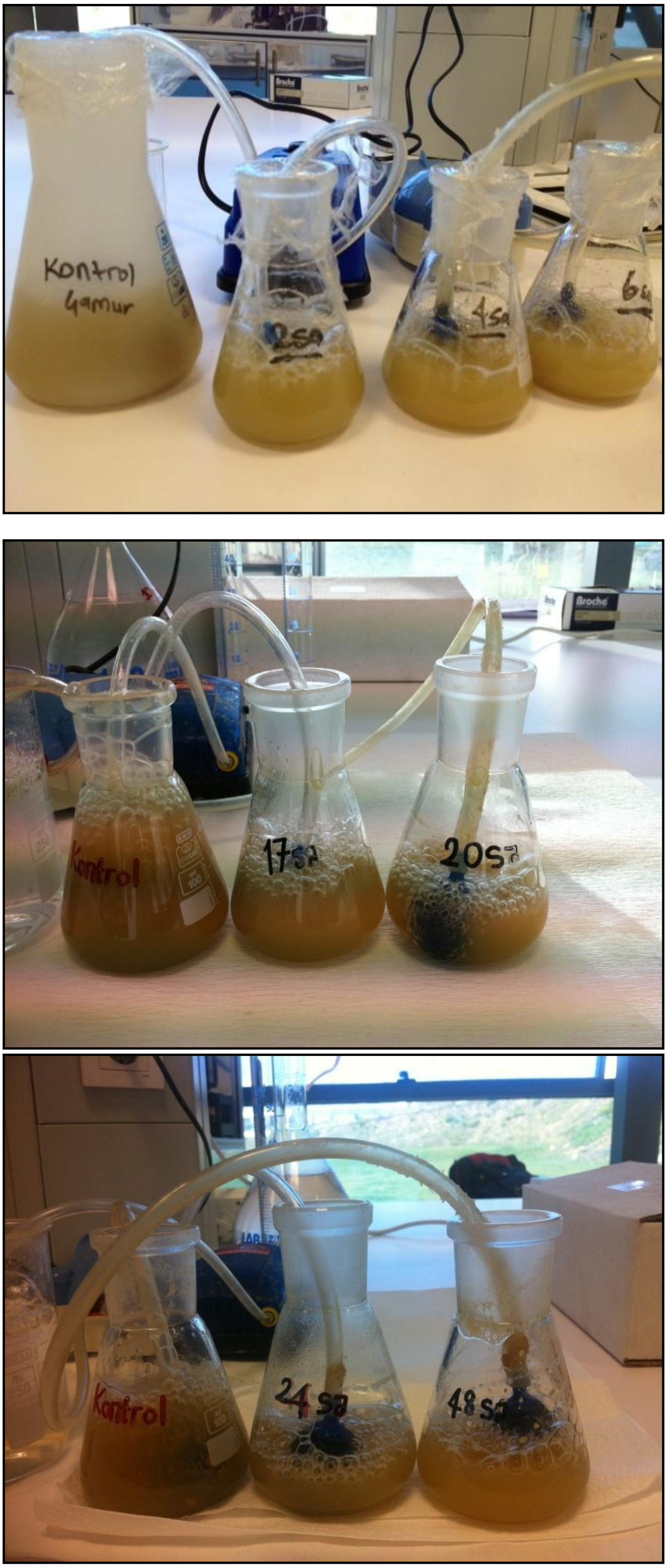



**Figure 3.10 :**Experimental setup for short-term exposure times.

### 3.4.3 Long-Term suspended and blended silver nanoparticle tests

After short-term experiments, the lab-scale MBR system was operated at semi-continuous to obtain the long-term effects of AgNP as suspended and blended. The lab-scale MBR were conducted at three different operation periods. At first operation period, the bare PES membrane in flat sheet module was used as control for compare with other periods. At second operation period, the bare PES membrane was extracted from MBR and the silver nanocomposite PES (AgNP-PES) membrane was immersed in same reactor. In the end of second period, AgNP-PES composite membrane was extracted from MBR and the bare PES membrane was immersed in the reactor and 10 mg AgNP/L was added to mixed liquor of the MBR on daily basis. Operation time of every period was 30 days. These different operation periods is summarized in Figure 3.11.

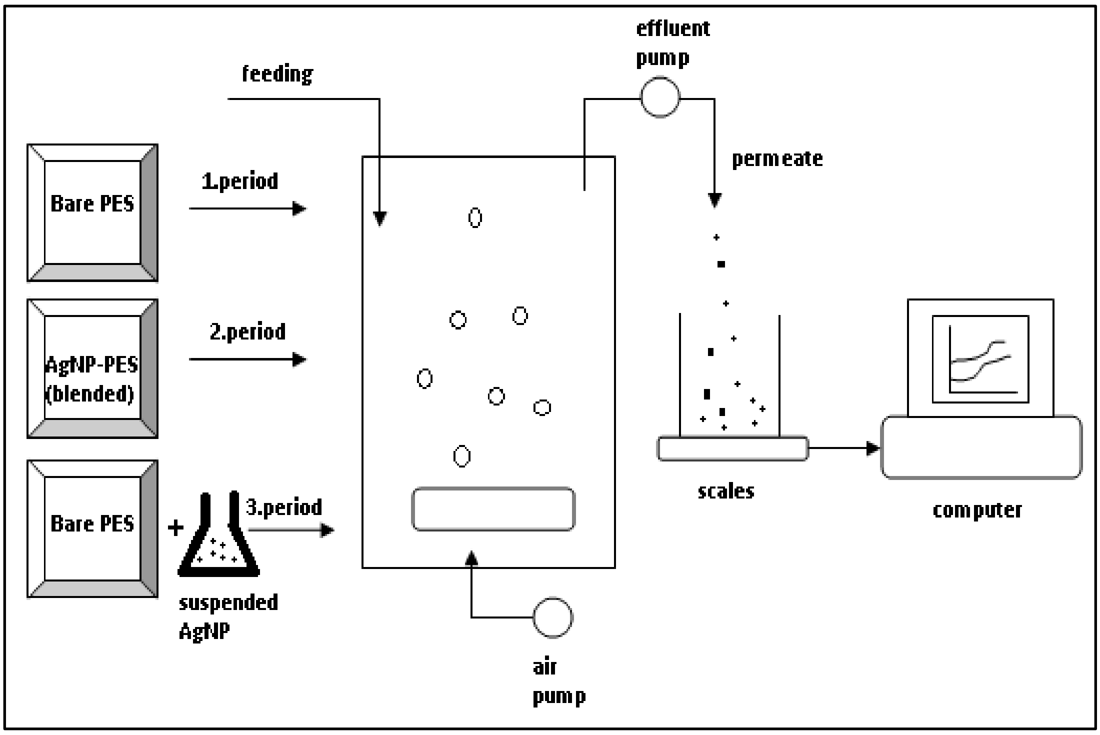



**Figure 3.11 :**The scheme of MBR operation periods.

The MBR was made of plexi-glassand had a total volume of 19 L. The flat sheet membrane had an effective filtration area of 14.6 $cm^2$. Coarse bubbleaeration was provided to the aerobic chamber through the orifices locatedat themodulebottomata constantflowrate of9.4 L/min to support bacterial growth and reducemembrane fouling.
The MBR system was fed by synthetic domestic wastewater containing 908 mg/L COD, 26 mg/L TP and 16 mg/L TKN. The composition of the synthetic domestic wastewater is given Table 3.3.

**Table 3.3 :** The composition of the synthetic domestic wastewater.

| **Chemicals** | **Amount (mg/L)** |
|---|---|
| Glucose | 1000 |
| Urea | 100 |
| $KH_2PO_4$ | 50 |
| $K_2HPO_4$ | 50 |
| $(NH_4)_2SO_4$ | 50 |
| $MgSO_4.7H_2O$ | 50 |
| $NaHCO_3$ | 250 |

In the every period, the activated sludge filtration performances of the membrane were monitored as total permeate volumes throughout the day and in the end of day, permeate volumes that was recorded every 40 minutes were averaged ($J_{ave}$) and MLSS, $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$, EPS and SMP of activated sludge and SMP of permeate analyses were carried out at every day. Once a week, samples for COD, TKN and TP analyses taken from the permeate were determined according to the Standart Methods. Measurement matrix for long-term experiments is given Table 3.4.

**Table 3.4 :** Measurement matrix for long-term experiments

| Parameter | Measurement Matrix |
|---|---|
| $J_{ss}$ | Everyday |
| MLSS | Everyday |
| $OD_{sludge,supernatant,permeate}$ | Everyday |
| $EPS_{activated\ sludge}$& $SMP_{activated\ sludge}$ | Everyday |
| $SMP_{permeate}$ | Everyday |
| COD | Once A Week |
| TKN | Once A Week |
| TP | Once A Week |

## 4. EXPERIMENTAL RESULTS

### 4.1 The Effects of Short-Term Suspended Silver Nanoparticle Exposure

#### 4.1.1 The effects of different exposure times at constant concentration

In the first stage, the effects of different exposure times (2, 4, 6, 17, 20, 24, 48 hours) at 10 mg AgNP/L on fitration performance of bare PES membrane were examined and results of experiments are shown as a graph in Figure 4.1. As can be seen from the graph, the flux values of activated sludge with AgNP showed a increasing trend with increasing exposure time at low time values. The highest flux value was obtained at 6 h of exposure time. After that, the flux values decreased with increasing exposure time. From this result, it can be said that when the exposure time of suspended AgNP increased, bacterial metabolism tolerated adverse effects of AgNP. Also, activated sludge with AgNP had higher flux in comparison with activated sludge without AgNP at 6 and 17 hours exposure. Hence, exposure time obtained the highest flux at the same concentration was selected for experiments in the second stage.

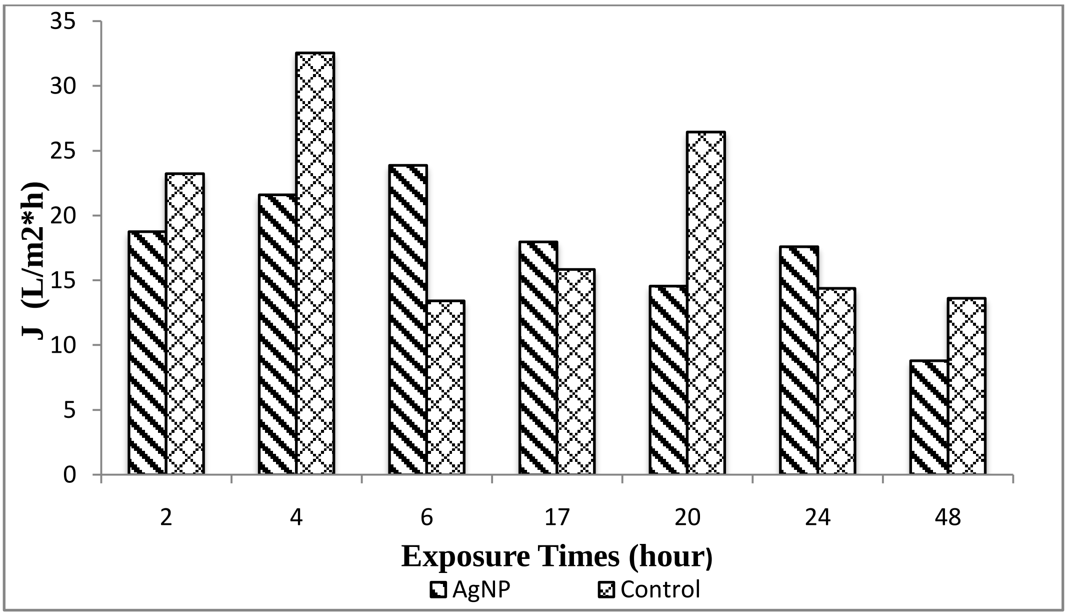



**Figure 4.1 :** Activated sludge containing 10 mg AgNP/L fitration performance of bare PES membrane in the short-term experiments.

Activated sludge with AgNP and activated sludge without AgNP were similar with respect to OD values (Figure 4.2), there was not a dramatic change for all exposure times.

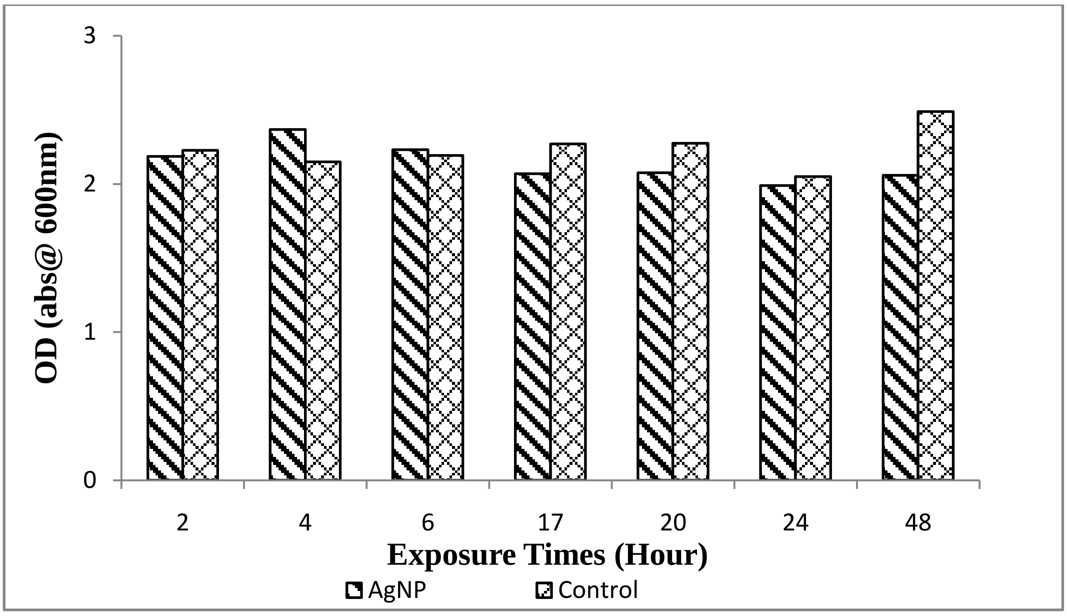
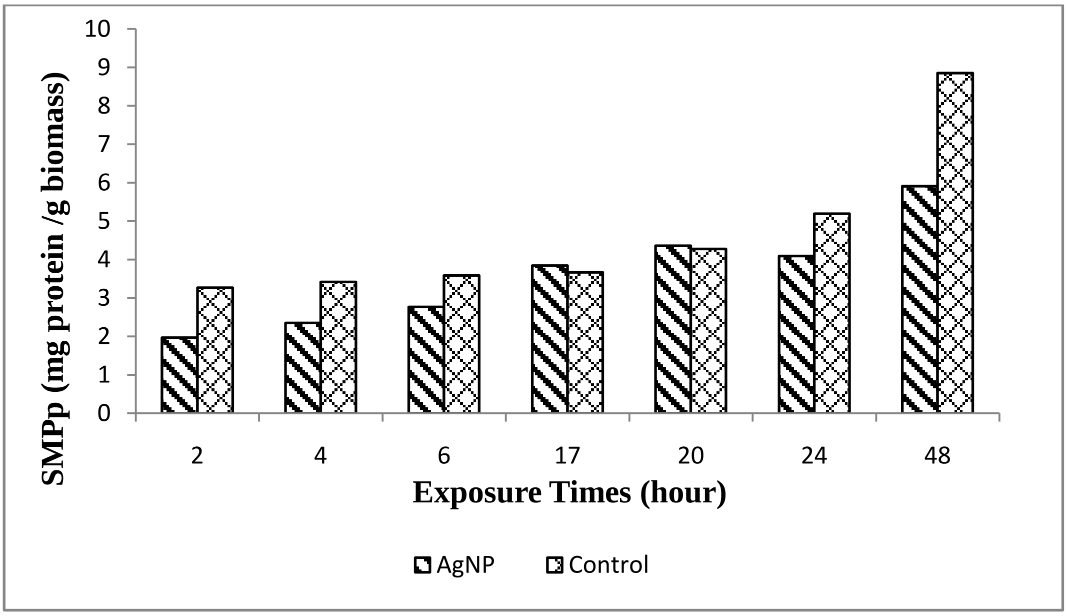


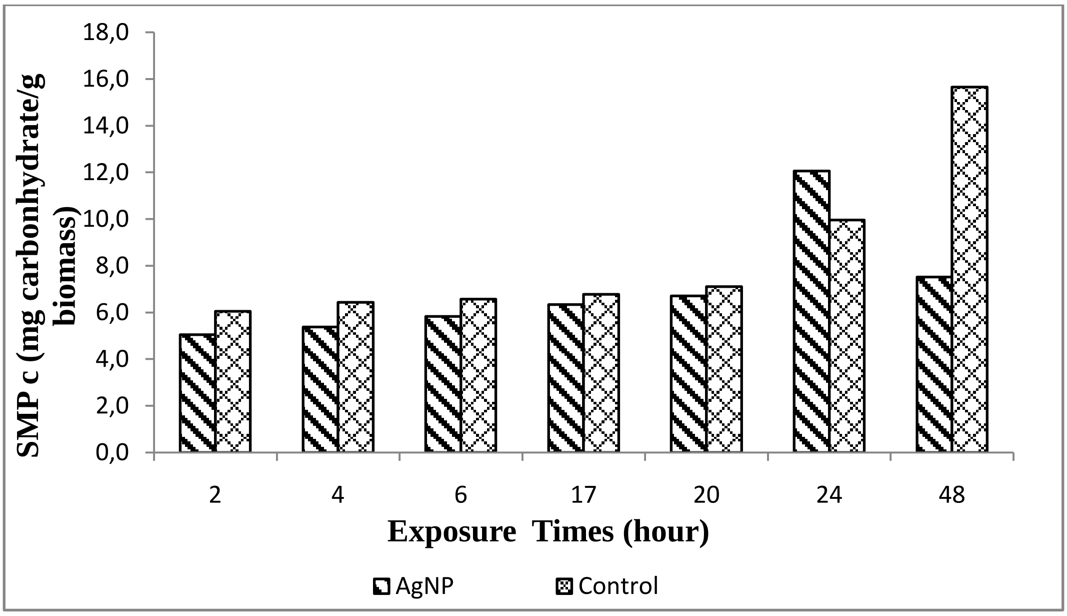

**Figure 4.2 :** OD values for short-term exposure (all exposure times) at 10 mg AgNP/L.

EPS and SMP analyses were carried out and results of experiments are shown as a graph in Figure 4.3 (a, b) and Figure 4.4 (a, b). As can be seen from the graphs of SMP, activated sludge with AgNP had lower $SMP_p$ and $SMP_c$ concentration compared with activated sludge without AgNP. Nevertheles, while exposure times increased, the $SMP_p$ and $SMP_c$ concentrations of activated sludge showed increase. That is to say, microorganisms showed resistance to toxic effects of AgNP exposure in time. According to numerical amounts, protein content of SMP has almost 3 mg protein/g biomass at 6




(a)

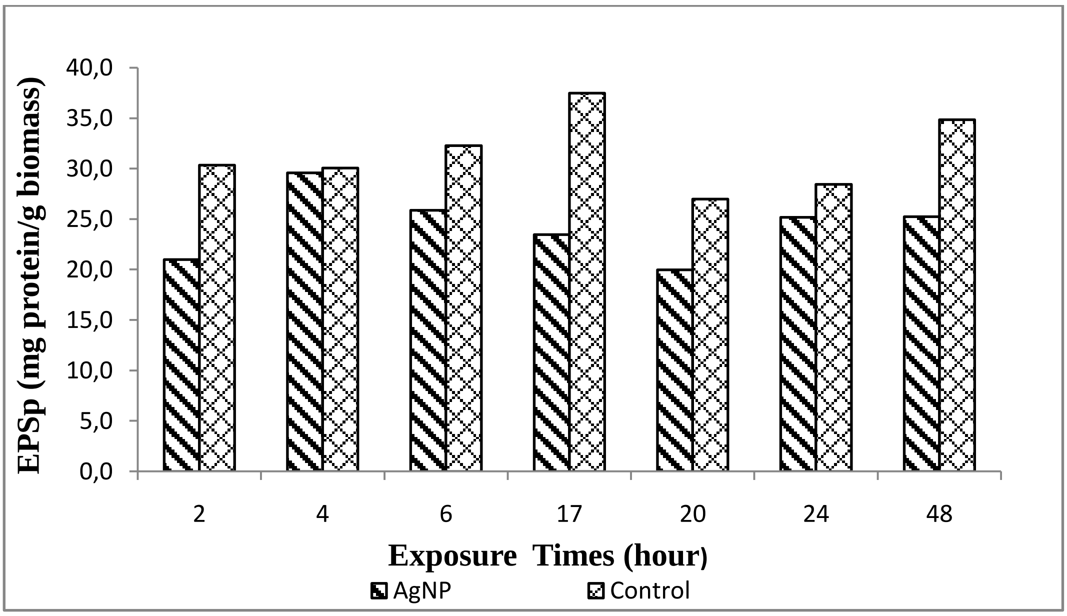
hours exposure but this value was higher at 17 hours exposure. Carbonhydrate concentration of SMP had the same values at 6 and 17 hours exposure times but protein amounts of SMP were lower than carbonhydrate amounts of SMP.



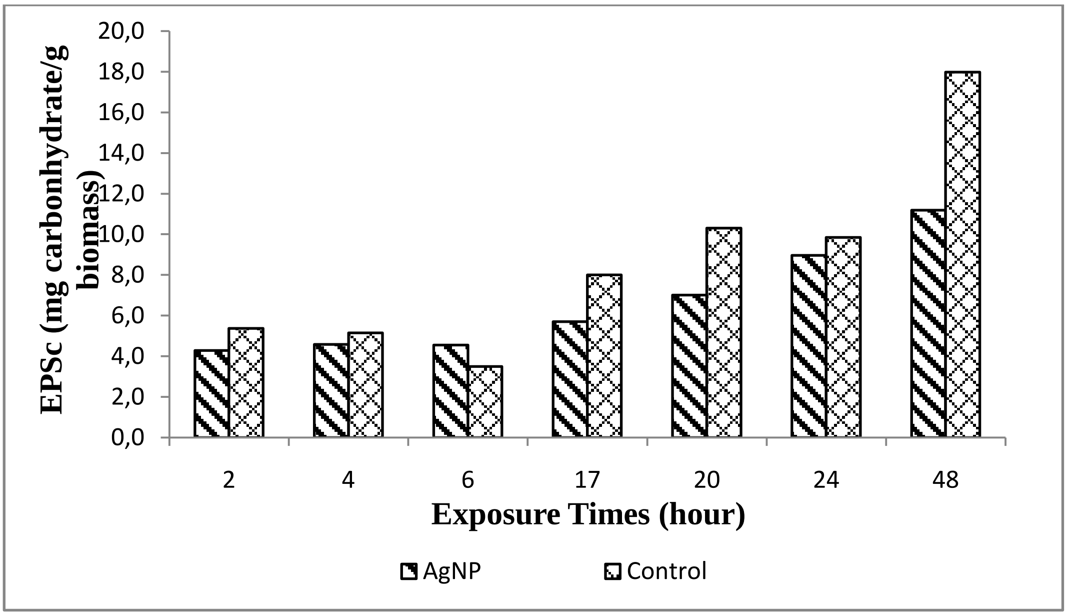

(b)

**Figure 4.3 :** The graphs of SMPanalysis for short-term exposure at 10 mg AgNP/L (a) $SMP_p$ (mg protein/gr biomass) (b) $SMP_c$ (mg carbohydrate/gr biomass).

As it is seen, $EPS_p$ and $EPS_c$ concentration of activated sludge with AgNP was lower than control activated sludge. Namely, the effect of AgNP was not different on EPS concentration. It means that AgNP in the activated slugde had adverse impact on bacterial products.




(a)




(b)

**Figure 4.4 :** The graphs of EPSanalysis for short-term exposure at 10 mg AgNP/L. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

Protein concentration of EPS had much higher value according to protein content of SMP at 6 hours exposure. Protein amount of EPS was 26 mg protein/gr biomass but that of SMP was 3 mg protein/gr biomass. In the same way, protein concentration of EPS was higher than that of SMP at 17 hours exposure. These values had 4 and 23 mg protein/gr biomass, respectively. Because as mentioned before biological substances analyzes (extracellular polymeric substances - EPS) activated sludge from each experimental vessel was taken into a centrifuged tube and then the suspension was centrifuged (4000×g, 10min, 40C). The supernatant was decanted into another sterile tube and recentrifuged (13.200×g, 20min, 40C) to ensure complete removal of the suspended solids. The resultant supernatant by this physical extraction contained soluble carbohydrate and soluble protein, and was analyzed for soluble EPS content (Soluble Microbial Products).

However, carbonhydrate concentration of EPS was lower both 6 and 17 hours exposure than those of SMP. Numerically, carbonhydrate amount of EPS had 4 and 6 mg carbonhydrate/gr biomass at 6 and 17 hours exposure, respectively. However, carbonhydrate amount of SMP had 6 and 7 mg carbonhydrate/gr biomassat 6 and 17 hours exposure, respectively.

### 4.1.2 The effects of different concentration at constant exposure times

In the second stage of short-term exposure, 6 and 17 hours were studied in the different concentration (5, 2,5, 1 mg AgNP/L). The graph of activated sludge containing 5 mg AgNP/L fitration performance of bare PES is given Figure 4. 5. As it is seen from the graph, activated sludge with AgNP had higher flux compared with control activated sludge like concentration of 10 mg AgNP/L but while AgNP concentration was decreased permeate flux values was a slight decrease. That is to say, the effect of AgNP on filtration performance was related to its concentration.

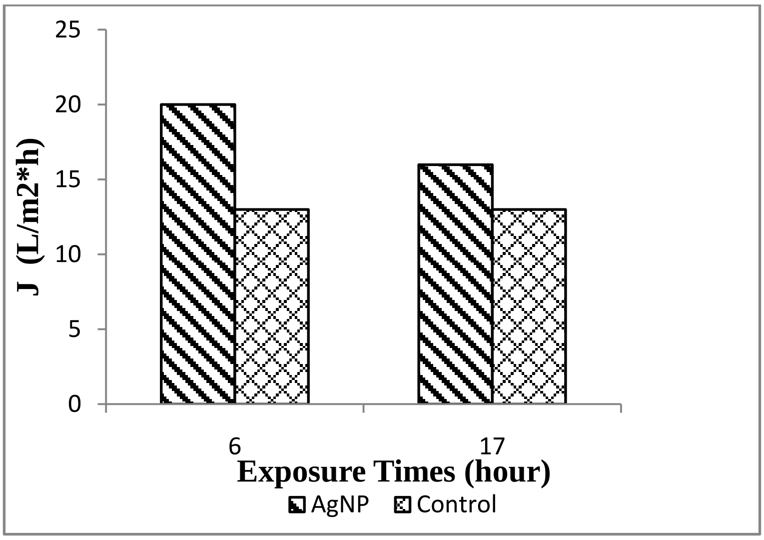



**Figure 4.5 :** Activated sludge containing 5 mg AgNP/L fitration performance of bare PES membrane in the short-term experiments.

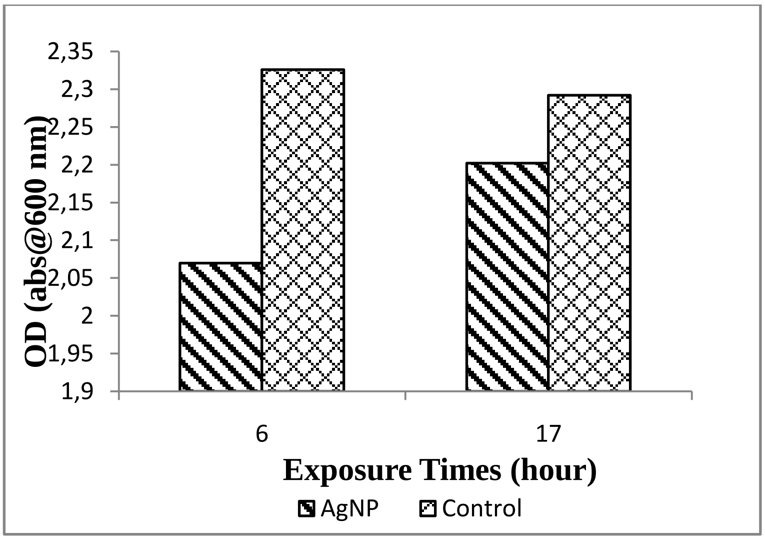
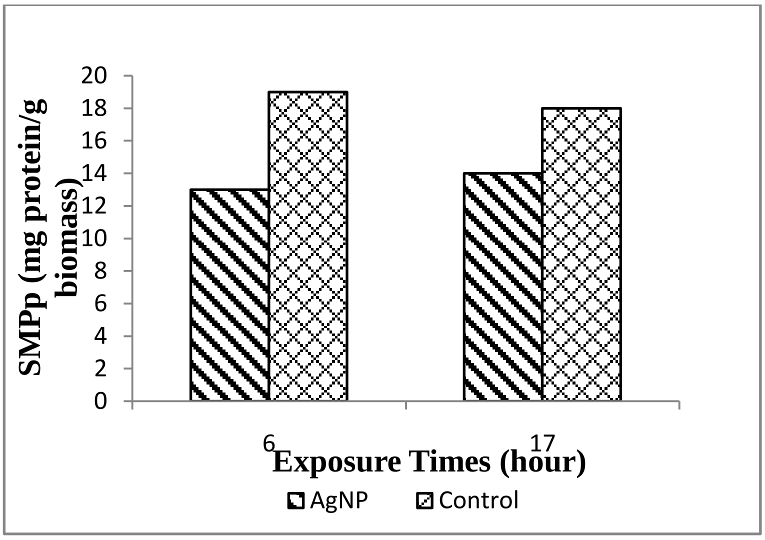
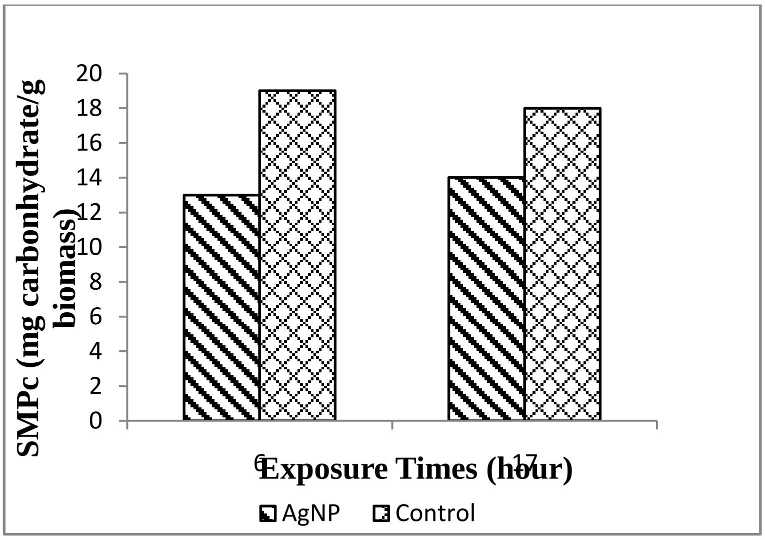



**Figure 4.6 :** OD values for short-term exposure (6 and 17 hours) at 5 mg AgNP/L.

The graphs of SMPand EPSanalyses at 5 mg AgNP/L is given Figure 4. 7 (a, b) and Figure 4. 8 (a, b). As it is seen from the graph of SMP, activated sludge with AgNP had lower $SMP_p$ and $SMP_c$ concentration compared with activated sludge without AgNP like 10 mg AgNP/L. However, in comparison with 10 mg AgNP/L, $SMP_p$ and $SMP_c$ concentration had higher values due to lower AgNP concentration.



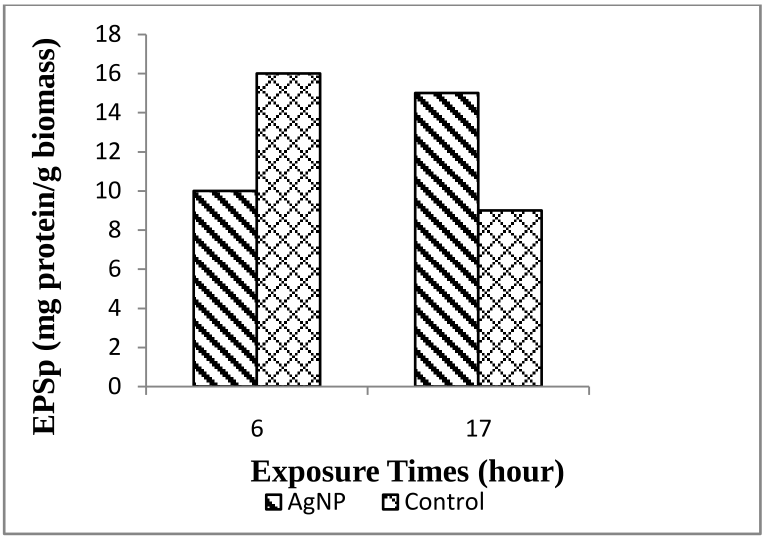

(a)



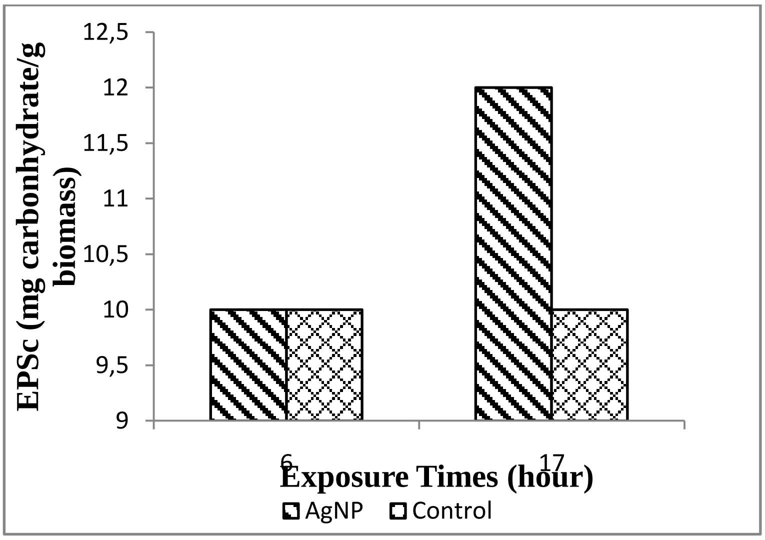

(b)

**Figure 4.7 :** The graphs of SMPanalysis for second stage of short-term exposure at 5 mg AgNP/L. (a) $SMP_p$ (mg protein/gr biomass) (b) $SMP_c$ (mg carbohydrate/gr biomass).

Differently from SMP graphs, when activated sludge was exposed to 5 mg AgNP/L for 17 hours, $EPS_p$ and $EPS_c$ concentration of activated sludge were observed a serious increase compared to activated sludge without AgNP.




(a)




(b)

**Figure 4.8 :** The graphs of EPSanalysis for second stage of short-term exposure at 5 mg AgNP/L. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

The graph of activated sludge containing 2.5 mg AgNP/L fitration performance of bare PES is given Figure 4. 9. As it is seen from the graph, activated sludge with AgNP had higher flux compared with control activated sludge like concentration of 10 and 5 mg AgNP/L. Nonetheles, permeate flux values at 5 and 2.5 mg AgNP/L were not observed noticeable change because there was remearkable change at 10 mg AgNP/L. Especially, permeate flux value of 6 hours exposure was an increase and highest permeate flux value was obtained with this exposure time.However, this flux had lower for other concentrations that was lower.

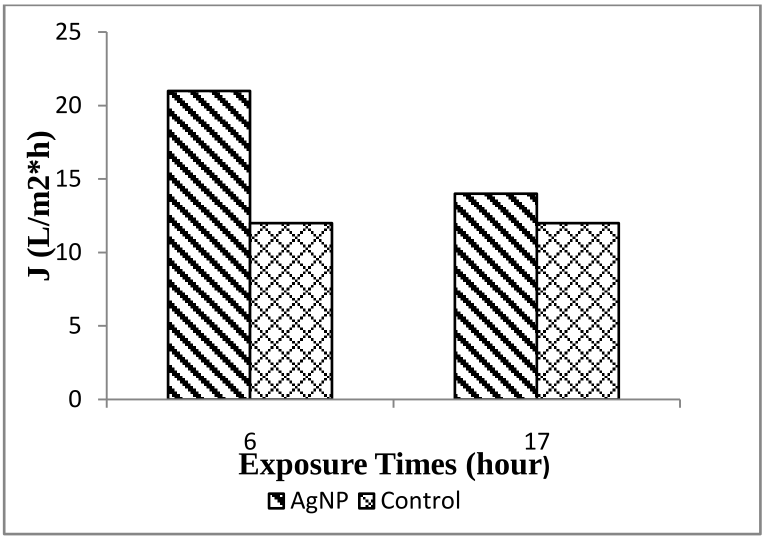



**Figure 4.9 :** Activated sludge containing 2.5 mg AgNP/L fitration performance of bare PES membrane in the short-term experiments.

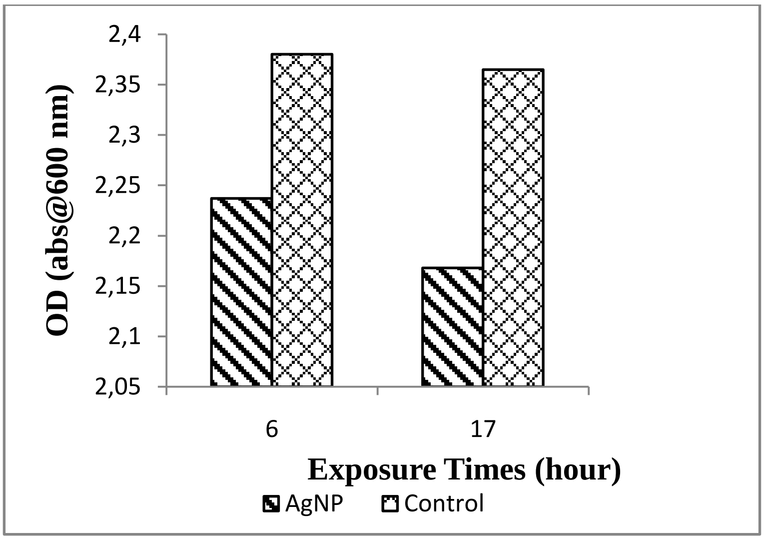
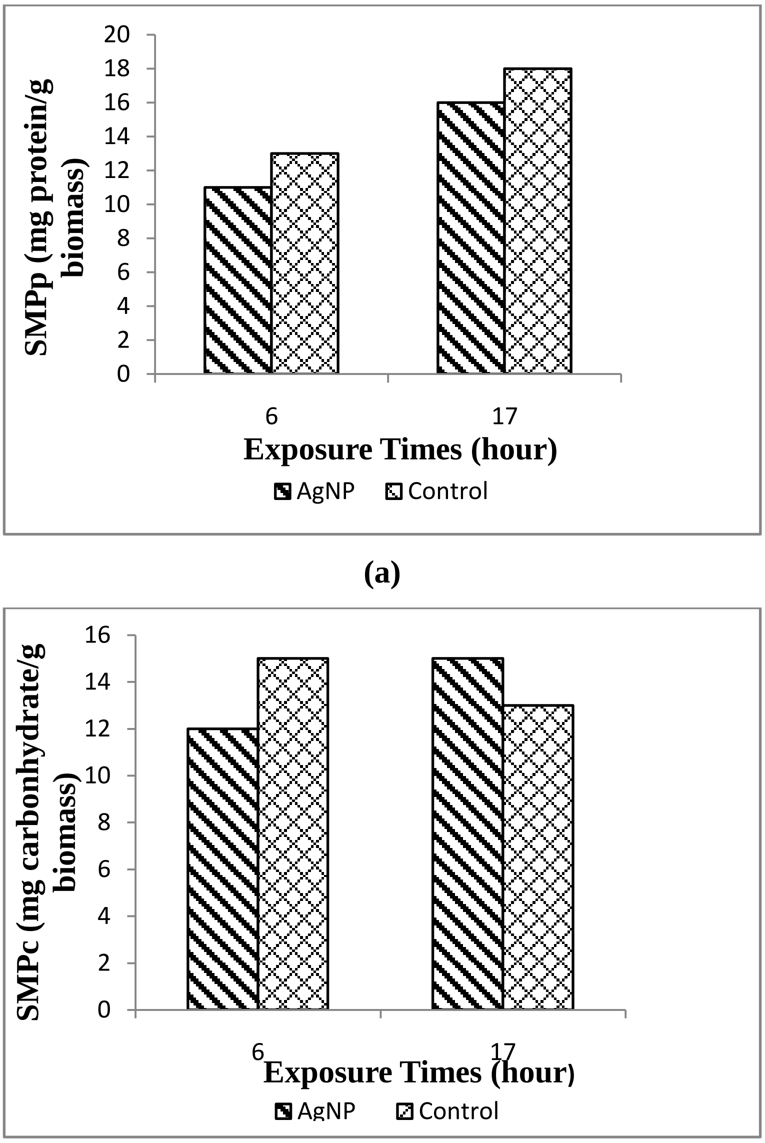



**Figure 4.10 :** OD values for short-term exposure (6 and 17 hours) at 2.5 mg AgNP/L.

The graphs of SMPand EPSanalyses at 2.5 mg AgNP/L is given Figure 4. 11 (a, b) and Figure 4. 12 (a, b). As it is seen from the graphs of SMP and EPS, as usual, activated sludge with AgNP had lower protein concentration of SMP and EPS and also carbonhydrate concentration of EPS concentration compared with activated sludge without AgNP like 10 and 5 mg AgNP/L. However, carbonhydrate concentration of SMPof actived sludge with AgNP at 17 hours exposure was higher than control activated sludge. Protein concentration of SMP has almost 3 mg protein/gr biomass value at 6 hours exposure at 10 mg AgNP/L. However, protein concentration of SMP has 13 and 11 mg protein/mg biomass values at 6 hours exposure at 5 and 2.5mg AgNP/L, respectively.

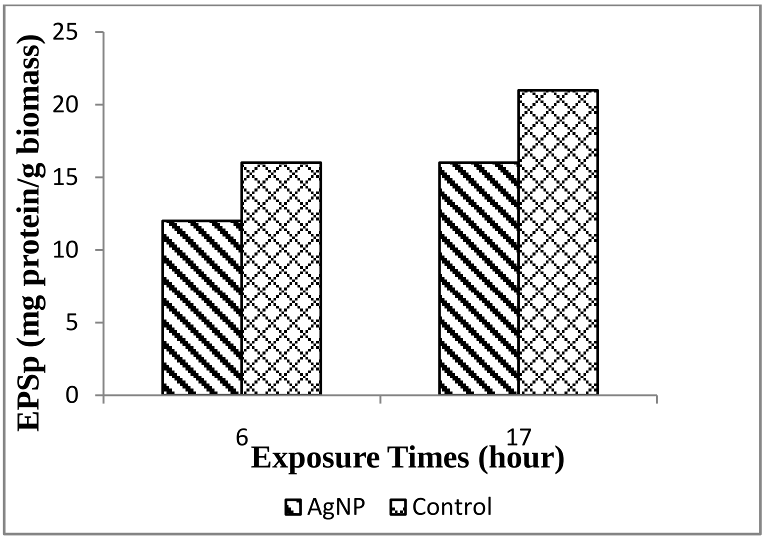
Carbonhydrate concentration of SMP has 6 mg protein/gr biomass value at 6 hours exposure at 10 mg AgNP/L. Notwithstanding, carbonhydrate concentration of SMP at 6 hours exposure has much more values for 5 and 2.5mg AgNP/L. These values were 13 and 12 mg protein/gr biomass, respectively. As it is seen from EPS results, protein concetration of EPS has 25 mg carbonhydrate/mg biomass value at 10 mg AgNP/L for 6 hours exposure. Nonetheless, there was a decrease at 6 hours exposure for 5 and 2.5mg AgNP/L. Because these values was 10 and 13 mg carbonhydrate/gr biomass, respectively.



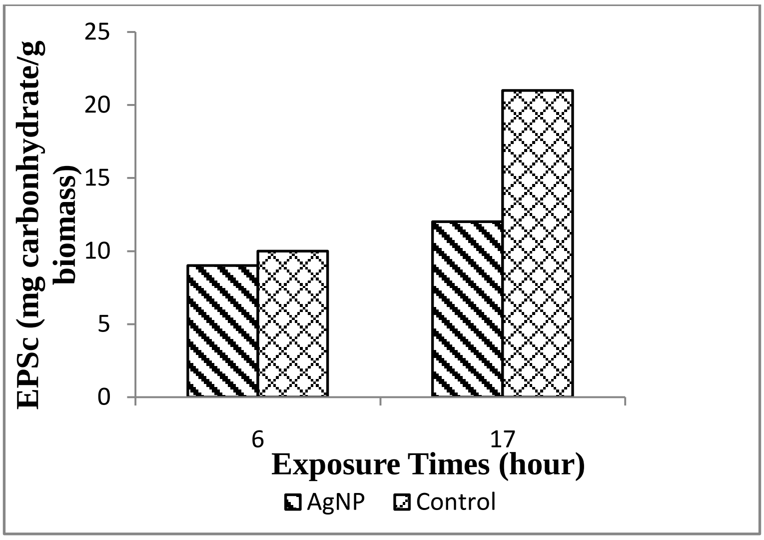

**(a)**

**(b)**

**Figure 4.11 :** The graphs of SMPanalysis for second stage of short-term exposure at 2.5 mg AgNP/L. (a) $SMP_p$ (mg protein/gr biomass) (b) $SMP_c$ (mg carbohydrate/gr biomass).




(a)




(b)

**Figure 4.12 :** The graphs of EPSanalysis for second stage of short-term exposure at 2.5 mg AgNP/L. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

Also, carbonhydrate concentration of EPS has 5 mg carbonhydrate/mg biomass at 6 hours exposure for 10 mg AgNP/L. However, this carbonhydrate content has higher value for more lower AgNP concentrations. According to numerical amounts, these values were 10 and 9 mg carbonhydrate/mg biomass for 5 and 2.5 mg AgNP/L.

The graph of activated sludge containing 1 mg AgNP/L fitration performance of bare PES is given Figure 4. 13. As it is seen from the graph, As it is seen from the graph, activated sludge with AgNP had higher flux compared with control activated sludge like concentration of 10, 5, 2.5 mg AgNP/L. Nonetheless, permeate flux values at 5, 2.5, 1 mg

AgNP/L were not observed noticeable change. Namely, filtration performance did not change at low AgNP concentration while exposure time was constant.

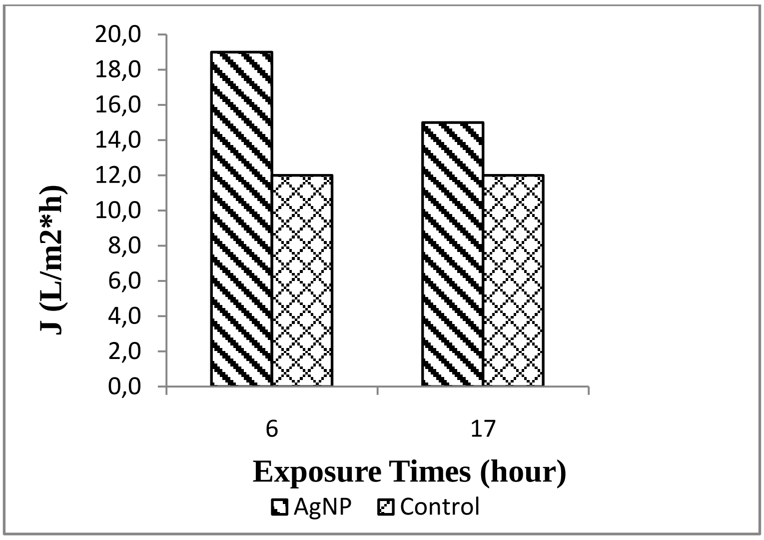



**Figure 4.13 :** Activated sludge containing 1 mg AgNP/L fitration performance of bare PES membrane in the short-term experiments.

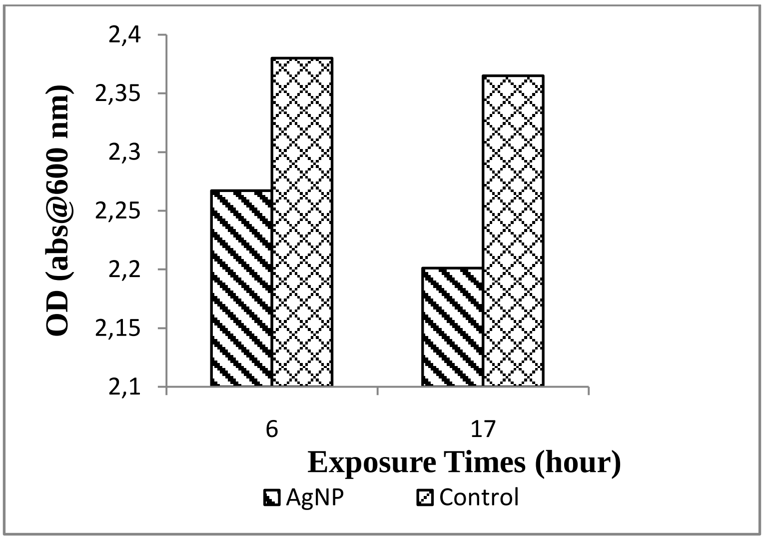
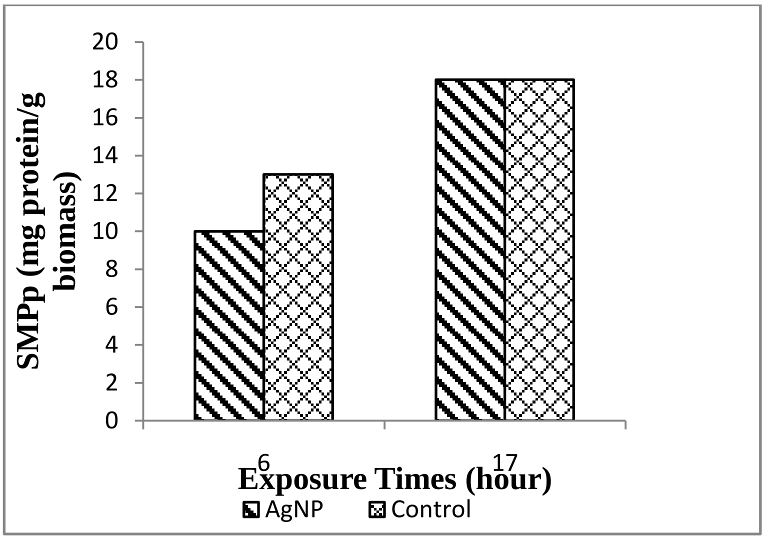
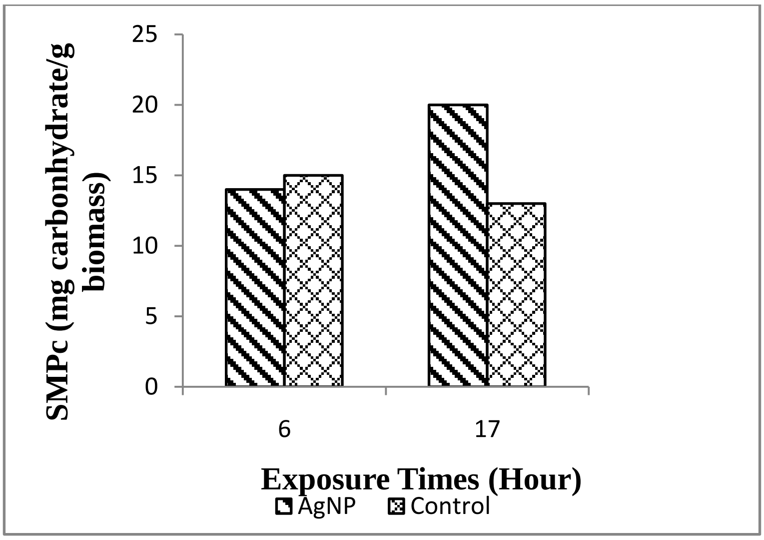



**Figure 4.14 :** OD values for short-term exposure (6 and 17 hours) at 1 mg AgNP/L.

The graphs of SMPand EPSanalyses at 1mg AgNP/L is given Figure 4.15 (a, b) and Figure 4. 16 (a, b). As it is seen from the graphs of SMP and EPS, as usual, activated sludge with AgNP had lower $SMP_p$ concentration compared with activated sludge without AgNP like 10, 5, 2.5 mg AgNP/L but $SMP_p$ concentration of activated sludge with AgNP the same as control activated sludge. Similar to 2.5 mg AgNP/L, $SMP_c$ concentration of actived sludge with AgNP at 17 hours was higher than control activated sludge. Also, diffently from the other graphs, $EPS_c$ of activated sludge with AgNP was higher concentration at 6 hours exposure than control activated sludge. Protein concentration of SMP was 10 mg/L and this value was lower than those of 5 and 2,5 mg AgNP/L but this value was higher than that of 10 mg AgNP/L. Carbonhydrate concentration of SMP had higher than all of the other concentrations. According to EPS results, protein content of EPS at 1 mg AgNP/L had lower value than 10 mg AgNP/L but this value was very close those of 5 and 2.5 mg AgNP/L. Also, carbonhydrate content of EPS had higher than other concentrations.

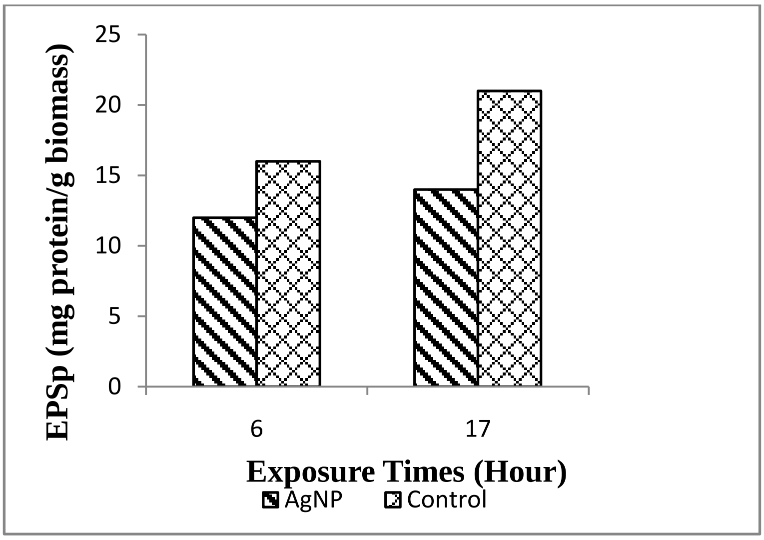



(a)

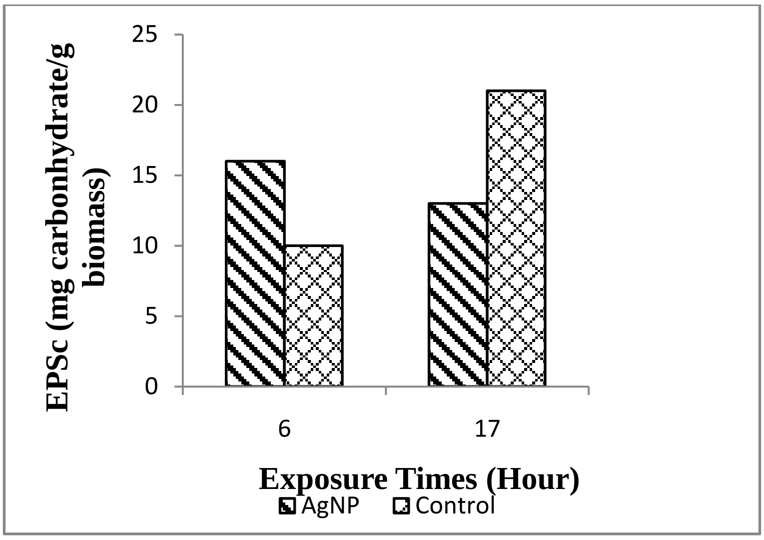



(b)

**Figure 4.15 :** The graphs of SMPanalysis for second stage of short-term exposure at 1 mg AgNP/L. (a) $SMP_p$ (mg protein/gr biomass) (b) $SMP_c$ (mg carbohydrate/gr biomass).




(a)




(b)

**Figure 4.16 :** The graphs of EPSanalysis for second stage of short-term exposure at 1 mg AgNP/L. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

In brief, in the first stage of short-term experiments (at the same concentration and the changing exposure times), positive effect of AgNP exposure on filtration performance was observed but while exposure times increased, filtration performance of bare PES membrane showed decrease. On the other hand, negative effect of AgNP exposure on bacterial products was observed but while exposure times increased, bacterial products showed increase. In the second stage of short-term experiment (at the same exposure time and the changing concentration), decrease AgNP concentrations caused filtration performace to decrease but bacterial products to increase.

## 4.2 The Effects of Long-Term Suspended and Blended Silver Nanoparticle Exposure

### 4.2.1 First period: Bare PES membrane test results

Firstly, bare PES membrane was used in the bioreactor as control system. MLSS experiments was carried out daily. The graph of MLSS is given in Figure 4.17. As it is seen from graph, a decreasing trend for MLSS concentration was observed. The MLSS concentration of activated sludge taken from MBR were averagely found as4702 mg/L in the first period. Although sludge was not removed from membrane bioreactor, MLSS concentration had a decreasing trend. This results showed that hydrolize occurs in the membrane bioreactor. However, a decrease of MLSS concentration was not observed for other two periods.

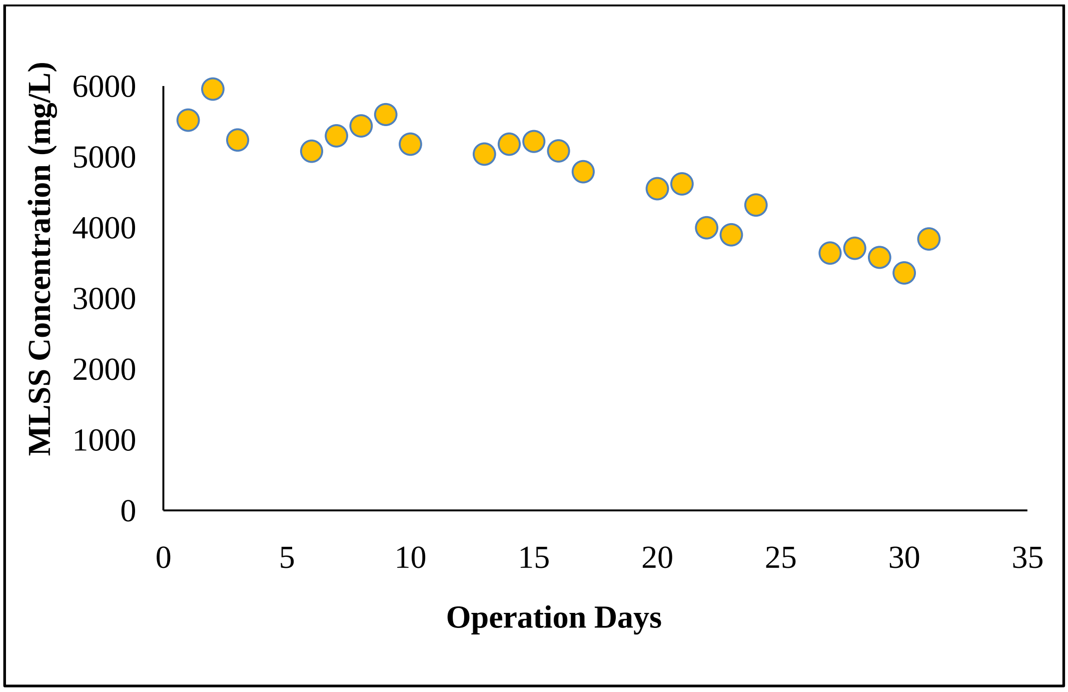



**Figure 4.17 :** The MLSS concentration values during first period.

The graphs of $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$ are given in Figure 4. 18. As it is seen from graph, the supernatant test results of the mixed liquor taken from the MBR enables us to learn about the settling properties of the sludge. As it is seen from $OD_{supernatant}$ graph, $OD_{supernatant}$ had relatively low values. It means that, the settling properties of the sludge was very good. As it is seen from $OD_{permeate}$ graph, the results of OD samples taken from the permeate of the MBR were averagely found as0,002. OD value of activated sludge had no remarkable change and generally its values were in the range of 2 and 2.5 properly.

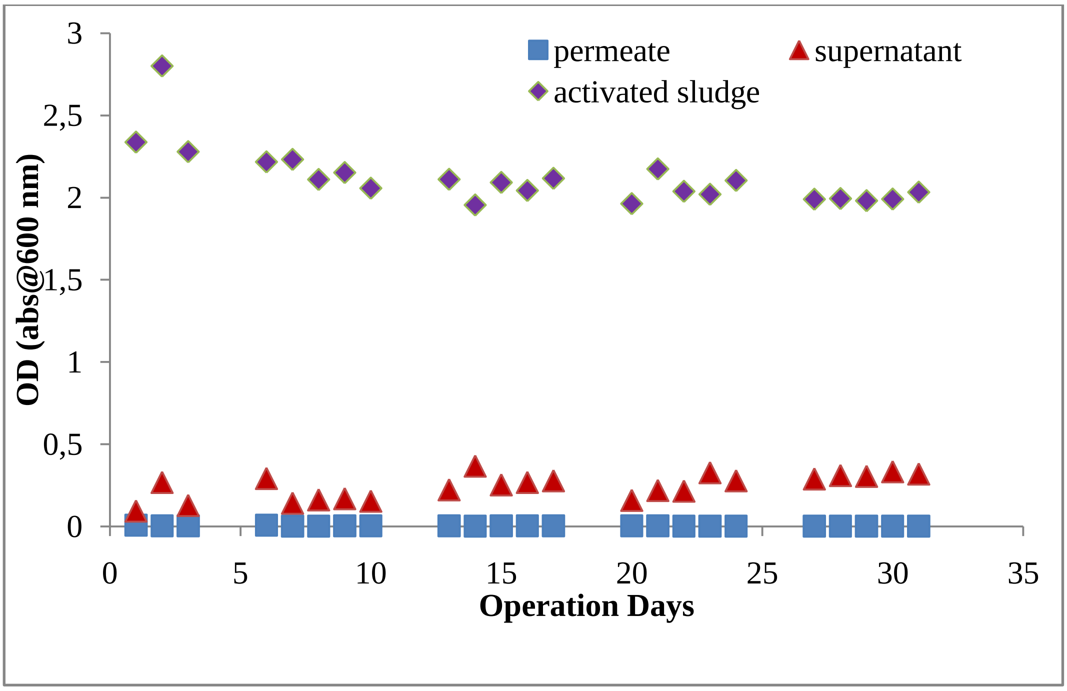
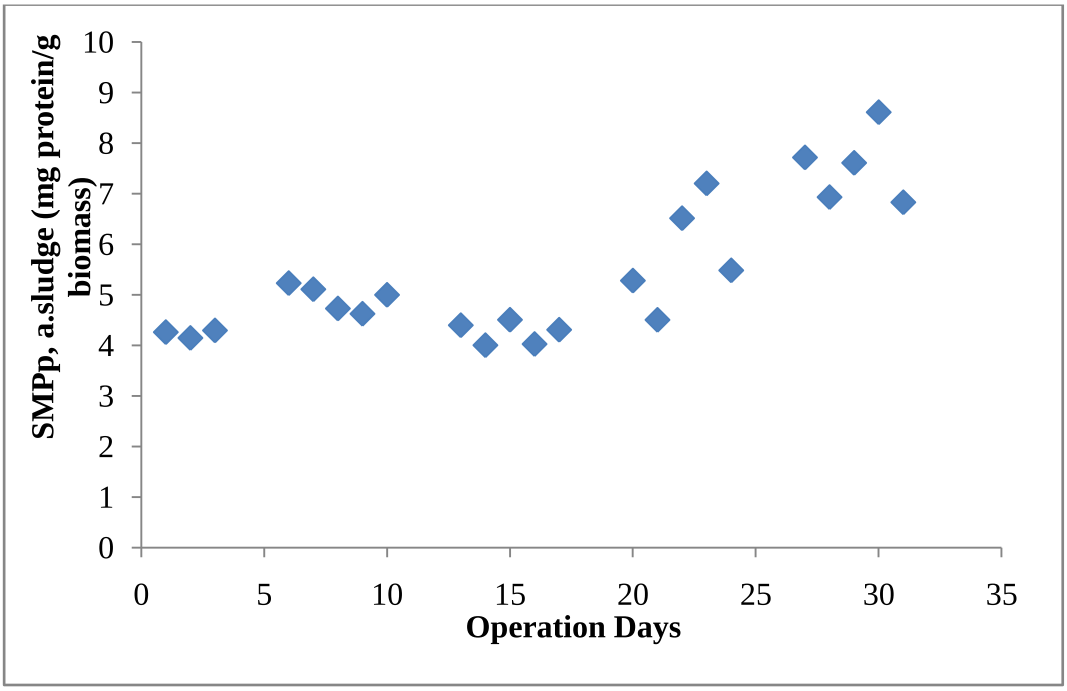



**Figure 4.18 :** The $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$ values during first period.

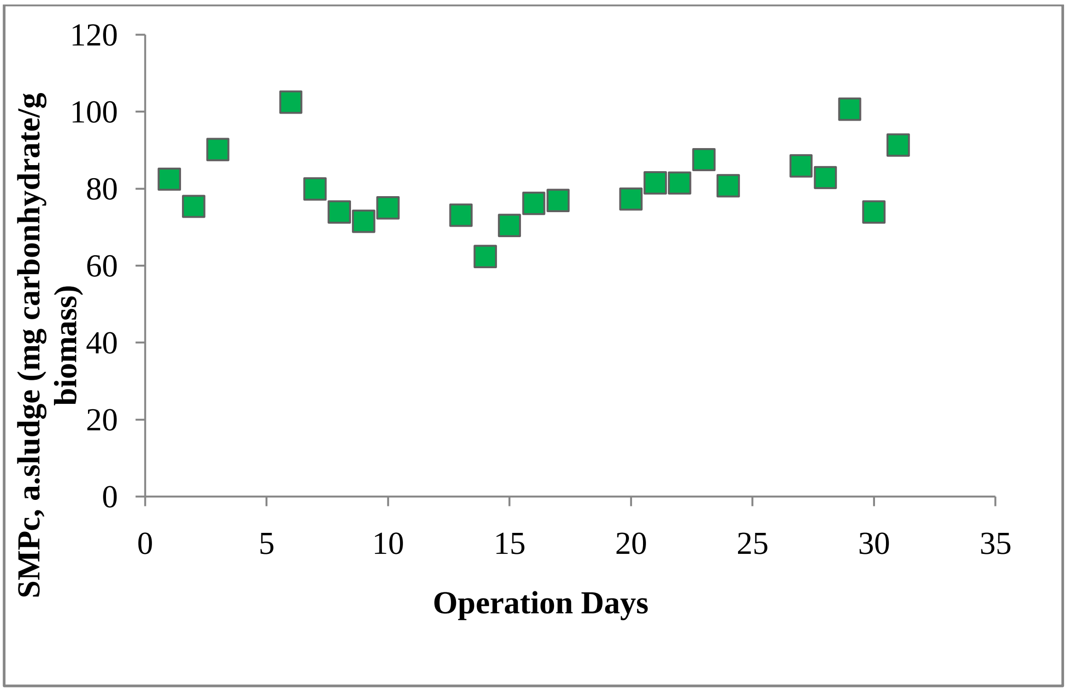
SMP analysis was carried out for active sludge taken from MBR and permeate. For this, sample of the activated sludge was taken at the beginning of day. Namely, before membrane was not immersed to bioreactor. Sample of the permeate was taken by the end of the day. Namely, after collected enough permeate flux that is 1000 ml, sample of permate was taken for SMP and EPS experiments. The graphs of SMP analyses are given in Figure 4. 19 (a-d). As it is seen from graph (a), despite the similar values in the first weeks of operation time, an increase was observed in the $SMP_p$ concentration of actived sludge over time. As it is seen from graph (b), the $SMP_c$ concentration of actived sludge had no noticeable change; hence, it was in the range of 60-100 mg carbohydrate/gr biomass and average value of carbonhydrate concentration of $SMP_{active\ sludge}$ was 80 mg carbohydrate/gr biomass. Also, average value of protein concentration of $SMP_{activated\ sludge}$concentrationswas 6 mg protein/g biomass in the first period.

As it is seen from graph (c), the protein concentration of $SMP_{permeate}$ was lower than the protein concentration of $SMP_{active\ sludge}$ and it means that bare PES membrane could keep the protein and average value of protein concentration of $SMP_{permeate}$ was 4 mg protein/g biomass.

As it is seen from graph (d), the carbonhydrate concentration of $SMP_{permeate}$ was similar to the carbonhydrate concentration of $SMP_{active\ sludge}$ taken from MBR. Moreover, Both had the same as avegare values that was 80 mg carbohydrate/gr biomass. It means that the membrane could not keep the carbonhydrate.Because, carbonhydrate and protein amounts should be lower in the permeate samples by comparison with activated sludge samples of membrane bioreactor.

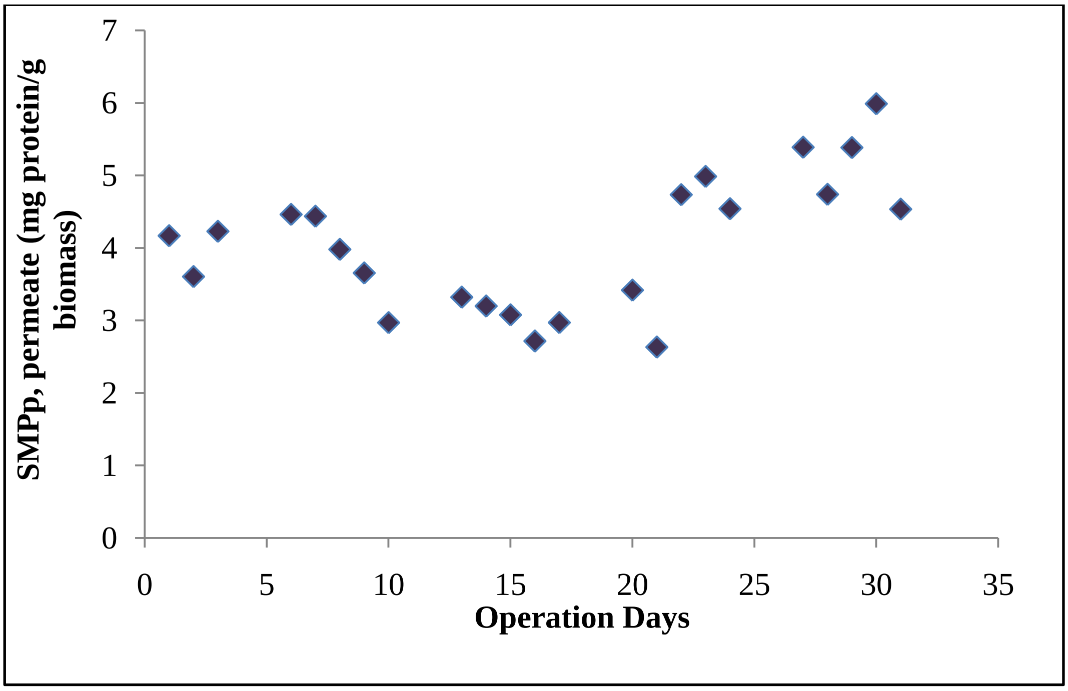



(a)

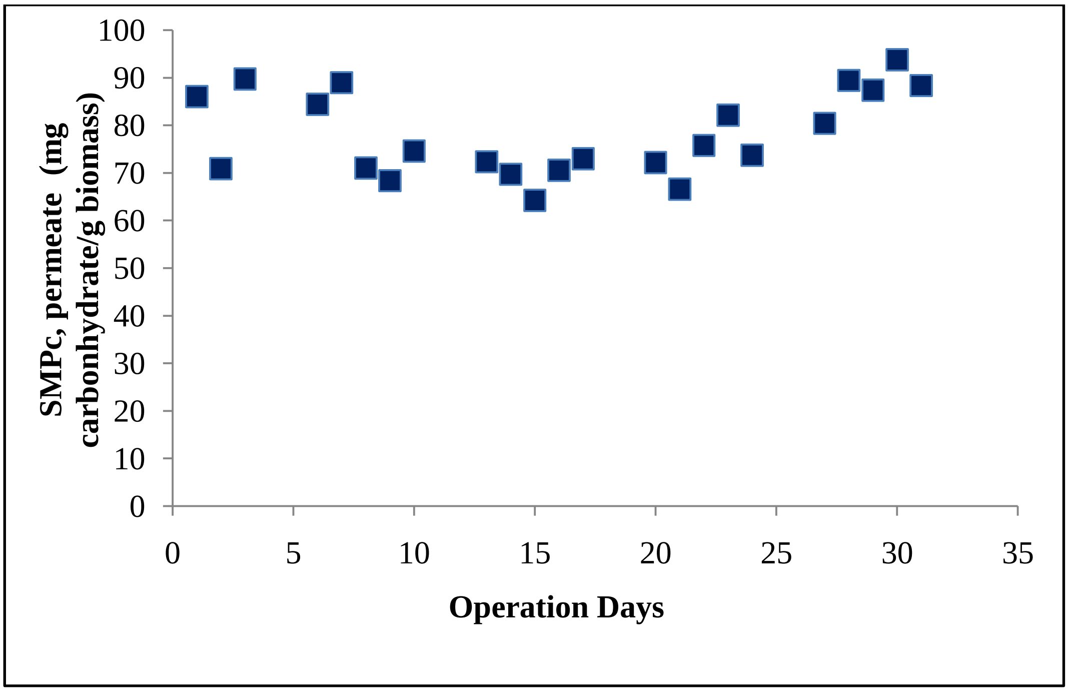



(b)

**Figure 4.19 :** The graphs of $SMP_{actived\ sludge}$ analysis during first period. (a) $SMPp_{,\ a.\ sludge}$ (mg protein/gr biomass) (b) $SMP_{c,\ a.sludge}$ (mg carbohydrate/gr biomass).



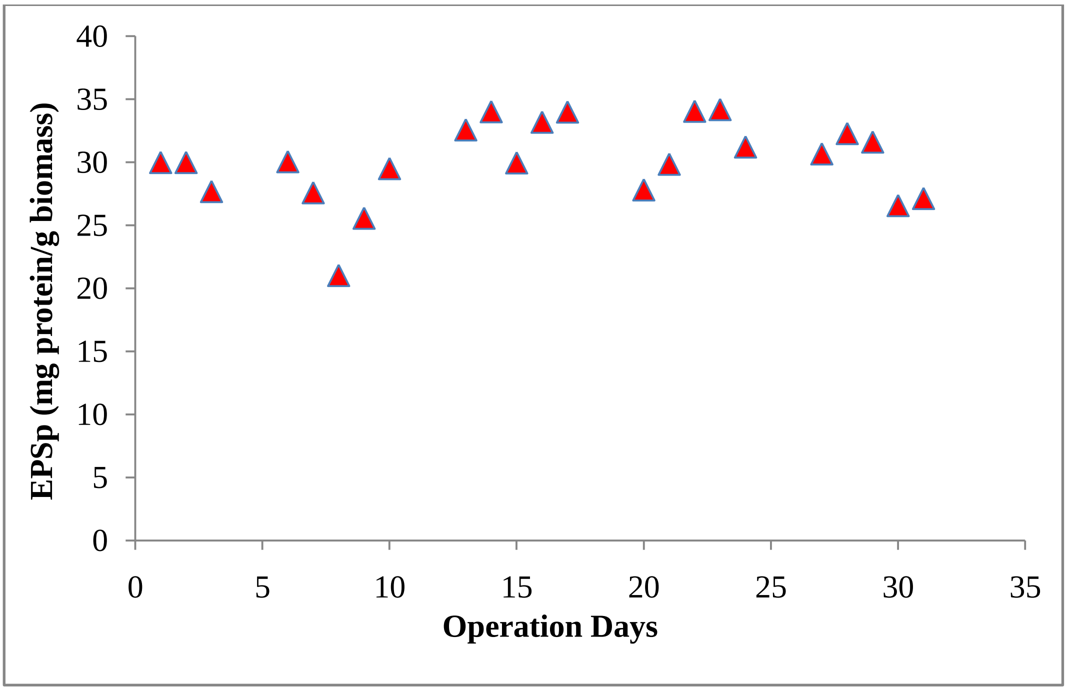

(c)



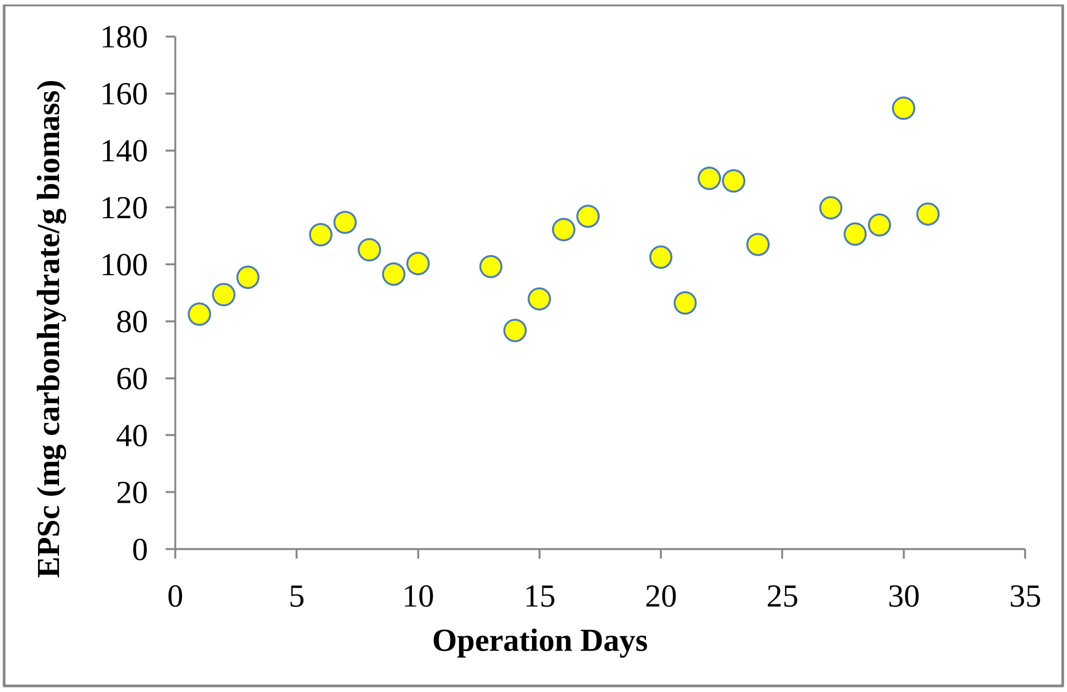

(d)

**Figure 4.19 (continued) :**The graphs of $SMP_{permeate}$ analysis during first period. (c) $SMP_{p,\ permeate}$ (mg protein/gr biomass) (d) $SMP_{c,\ permeate}$ (mg carbohydrate/gr biomass).

The graphs of EPS analyses are given in Figure 4. 20 (a,b). As it is seen from graph (a,b), there were not a dramatic increase and decrease in the rate of $EPS_p$ and $EPS_c$ concentrations. Average value of $EPS_p$ concentrationswas 30 mg protein/g biomass and that of $EPS_c$concentrationswas 110 mg carbohydrate/gr biomass in the first period.




(a)




(b)

**Figure 4.20 :** The graphs of EPS analysis during first period. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

The activated sludge filtration performance of bare PES membrane is given at Figure 4. 21. As it is seen from graph, a decresing trend was observed because of membrane fouling problem in time. In this period, $J_{ss}$ that is average permeate flux of the last five day was 7 $L/m^2*h$.

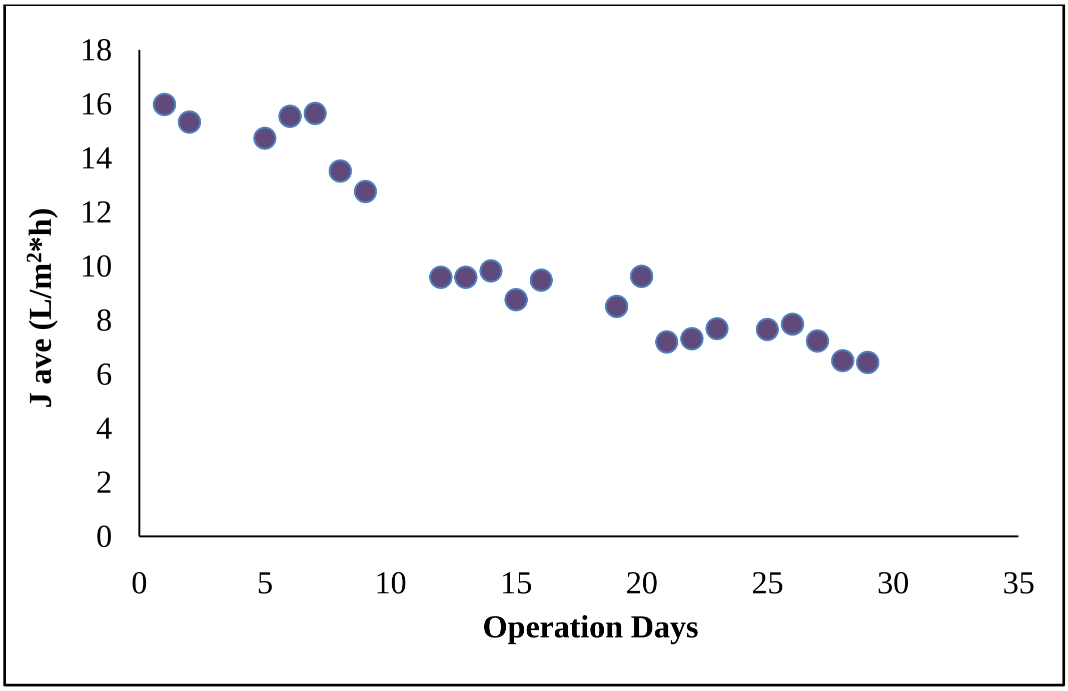



**Figure 4.21 :** The activated sludge filtration performance of bare PES membrane during first period.

The graph of COD analysis is given in Figure 4. 22. As it is seen graph, an icreasing trend was observed in the COD removal efficiency and average of COD removal efficiency was calculated as 96 % in this period.

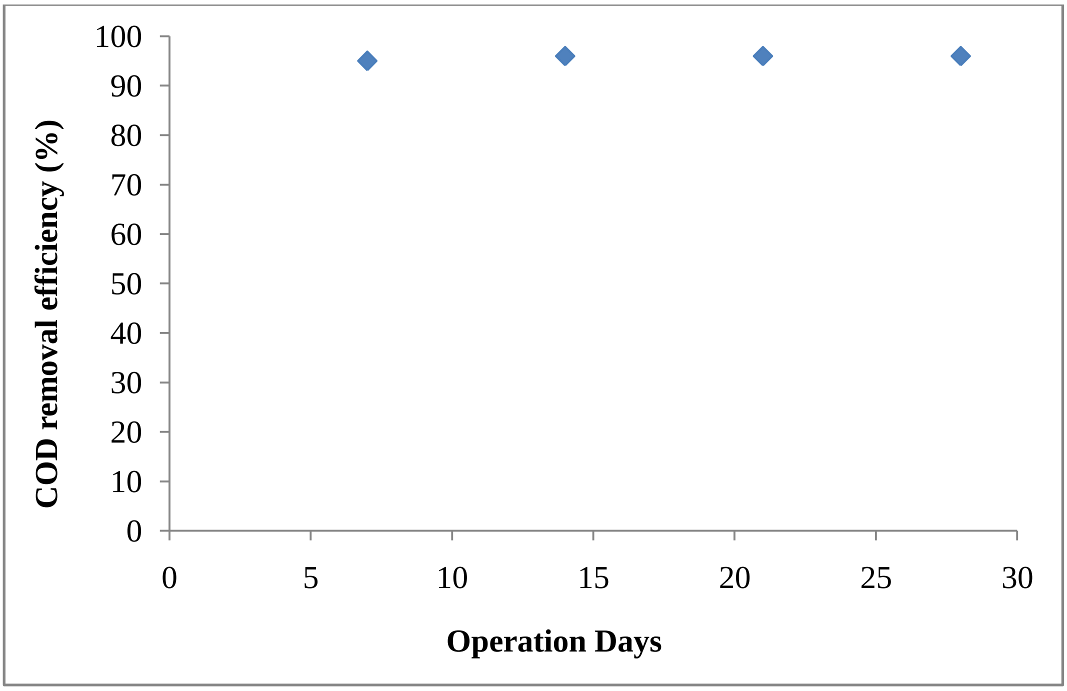



**Figure 4.22 :** The graph of COD removal efficiency during first period.

The graph of TKN and TP analysis is given in Figure 4. 23 and 4.24. Effluent TKN values was much the same during this period and TKN removal efficiency was 30 %. On the TP graphs, it is seen that, there was a decrease.

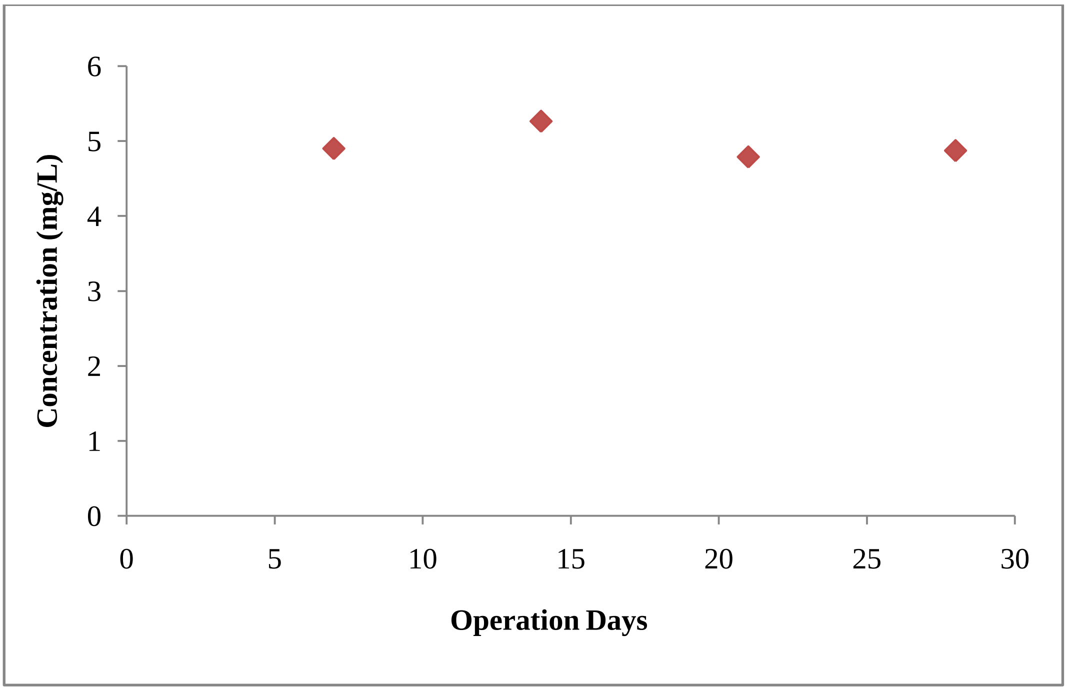



**Figure 4.23 :** The graph of TKN concentrations during first period.

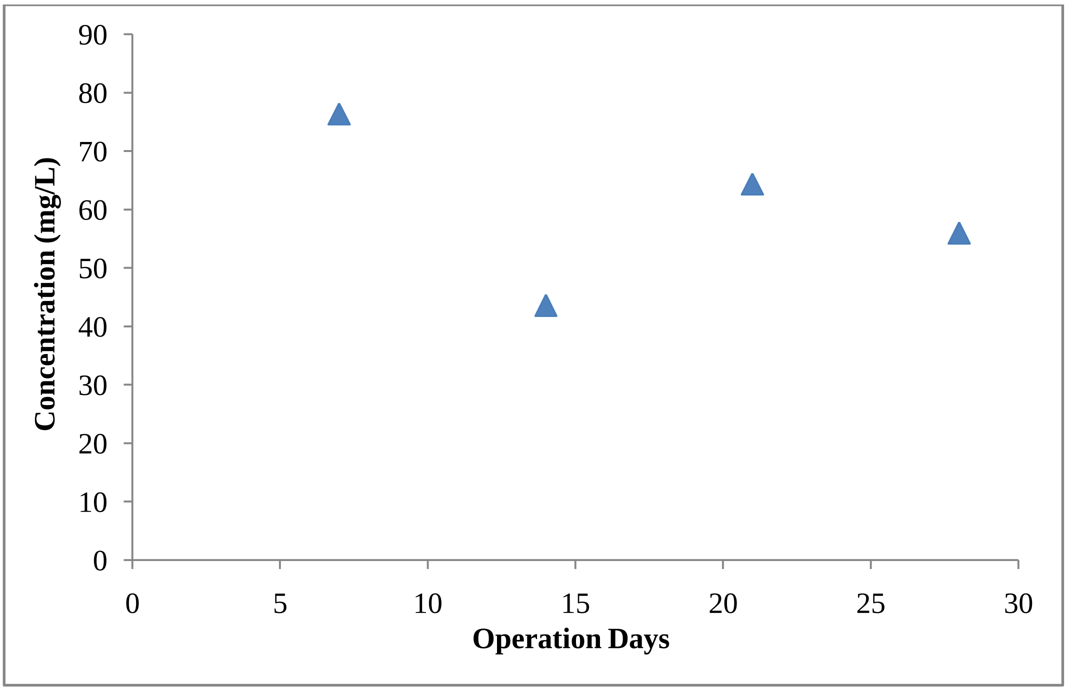



**Figure 4.24 :** The graph of TP concentrations during first period.

### 4.4.2 Second period: AgNP-PES composite membrane test results

The graph of MLSS is given in Figure 4. 25. As it is seen from graph, MLSS concentration was observed in the range of 4180-5500 mg/L. MLSS concentration did not changed remarkably in the second period compared to first period. The graph of MLSS concentration in the first period was more different than second period; therefore, a noticeable decrease was observed in the first period. The MLSS concentration of activated sludge taken from MBR were averagely found as4990 mg/L for second period.

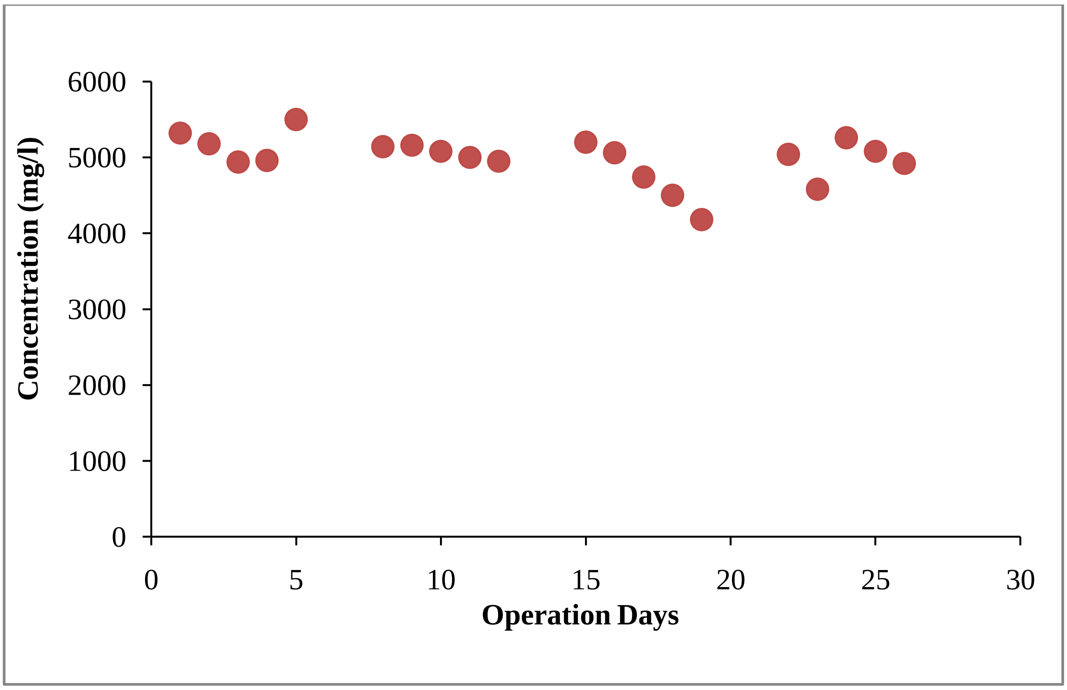



**Figure 4.25 :** The MLSS concentration values during second period.

The graphs of $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$ are given in Figure 4. 26. As it is seen from graph (a), the graph of $OD_{sludge}$ which is similar to graph of MLSS was observed. Its values were in the range of 2 and 2.5 like that of first period but these values were stable in this period differently from first period.

As it is seen from $OD_{supernatant}$ graph, $OD_{supernatant}$ had relatively low values in the second period like first period. This result indicated that settling properties of activated sludge were relatively good and it did not change in spite of usage of composite membrane with silver nanoparticles. As it is seen from $OD_{permeate}$ graph, the samples of OD taken from the permeate of the MBR values were averagely found as0,003 mg/L. this value was higher than that of first period. Although it is not a fundamental change, this amount of permeate of OD indicated that microorganism passed from the membrane.

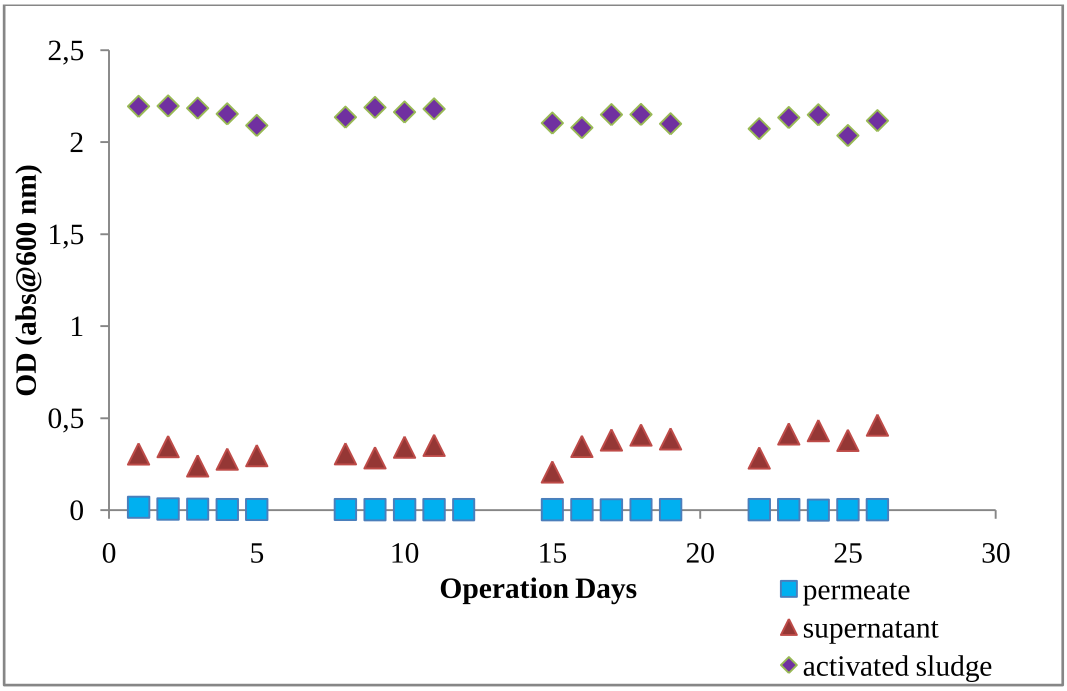
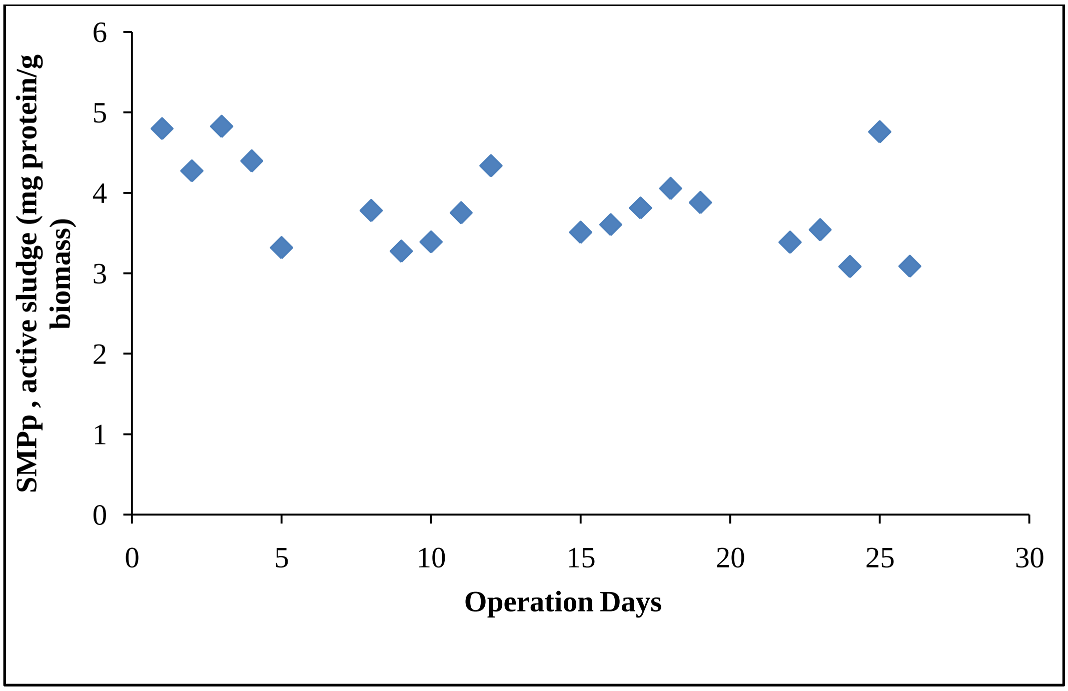
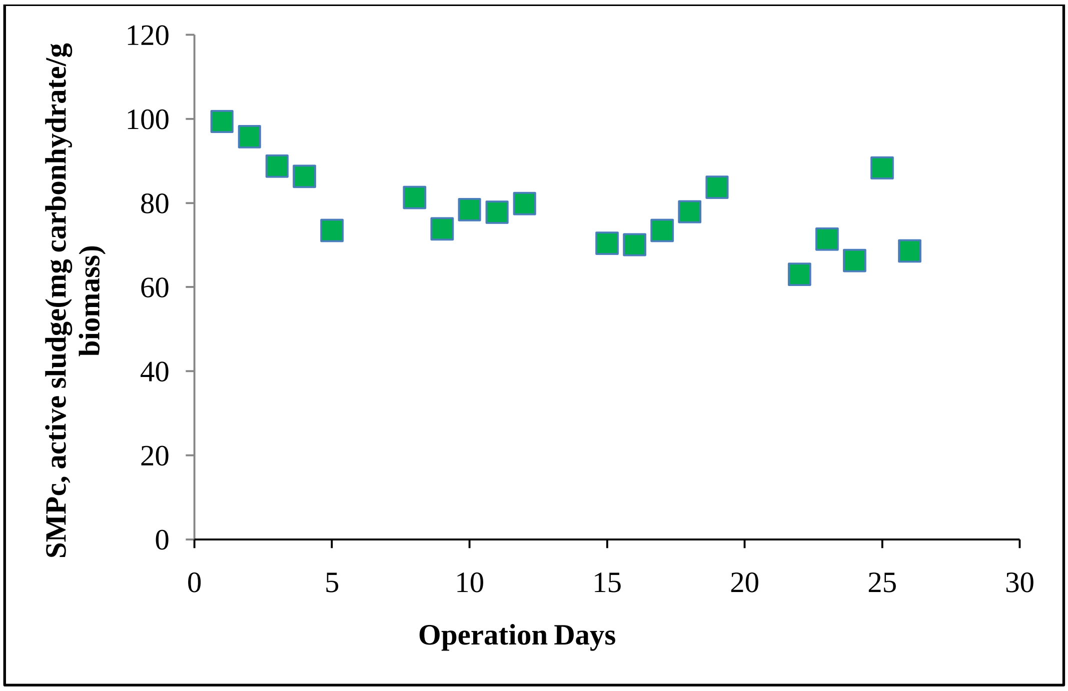



**Figure 4.26 :** The $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$ values during second period.

The graphs of SMP analysis are given in Figure 4. 27 (a-d). As it is seen from graph (a), in spite of high values in the first days of operation time, a decrease were observed in the $SMP_p$ concentration of actived sludge over time compared to first period. As it is seen from graph (b), a decrease was observed in the $SMP_c$ concentration of actived sludge. It was observed that when AgNP incorporated PES membranewas used, $SMP_p$ and $SMP_c$ concentrations of active sludge was lower than those of first period. Furthermore, according to average values, average $SMP_p$concentration was lower than that of first period but average $SMP_c$ concentrations was same at the both periods.As it is seen from graph (c), the protein concentration was a smaller range of $SMP_{permeate}$; moreover, it had steady state during period compared with $SMP_{p,\ active\ sludge}$. Its average value was 4 mg protein/gr biomass. Also, protein concentration of permeate of SMP was 4 mg protein/gr biomass. As it is seen from graph (d), the carbonhydrate concentration of $SMP_{permeate}$ was similar to that of $SMP_{activesludge}$ taken from MBR. According to average values, average $SMP_{p,\ permeate}$concentration was the same average $SMP_{p,\ activated\ sludge}$ as. As mentioned before, they had 4 mg protein/gr biomass averagely. That is to say, PES composite membrane with AgNP could not keep protein. Average $SMP_{c,\ permeate}$concentration was lower than average $SMP_{c,\ activated\ sludge}$ concentrations. It means that composite membrane with AgNP could keep carbonhydrate. Compared with average values of first period, both average $SMP_{p,\ permeate}$concentrations had the same values.However, average $SMP_{c,\ permeate}$ concentration in the second period was lower than that of first period.

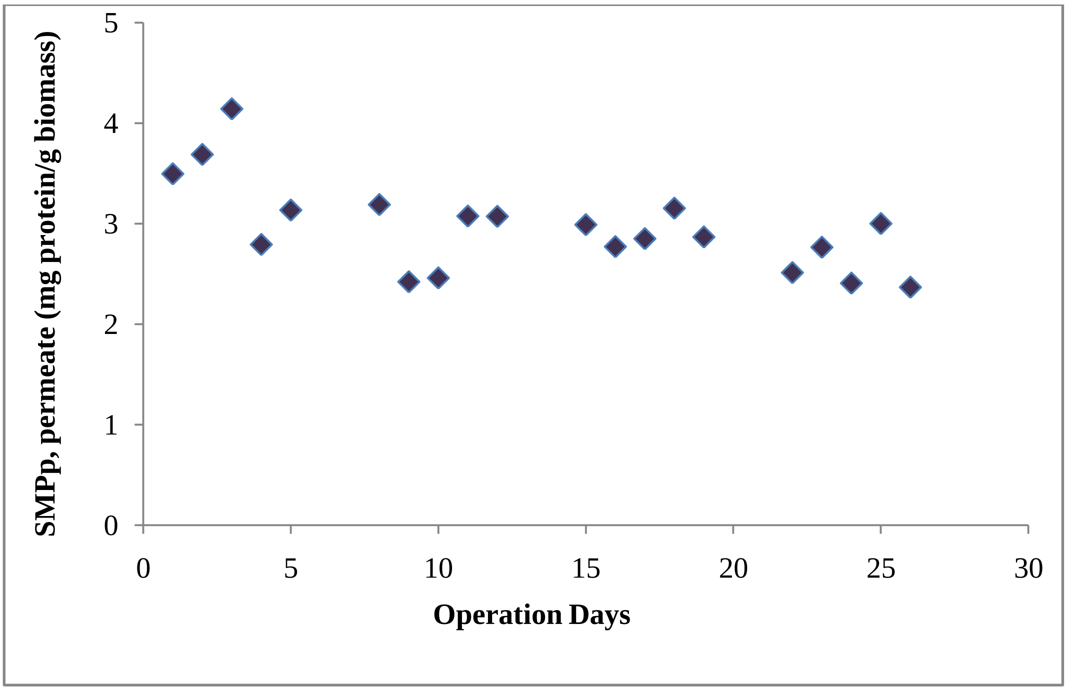



(a)

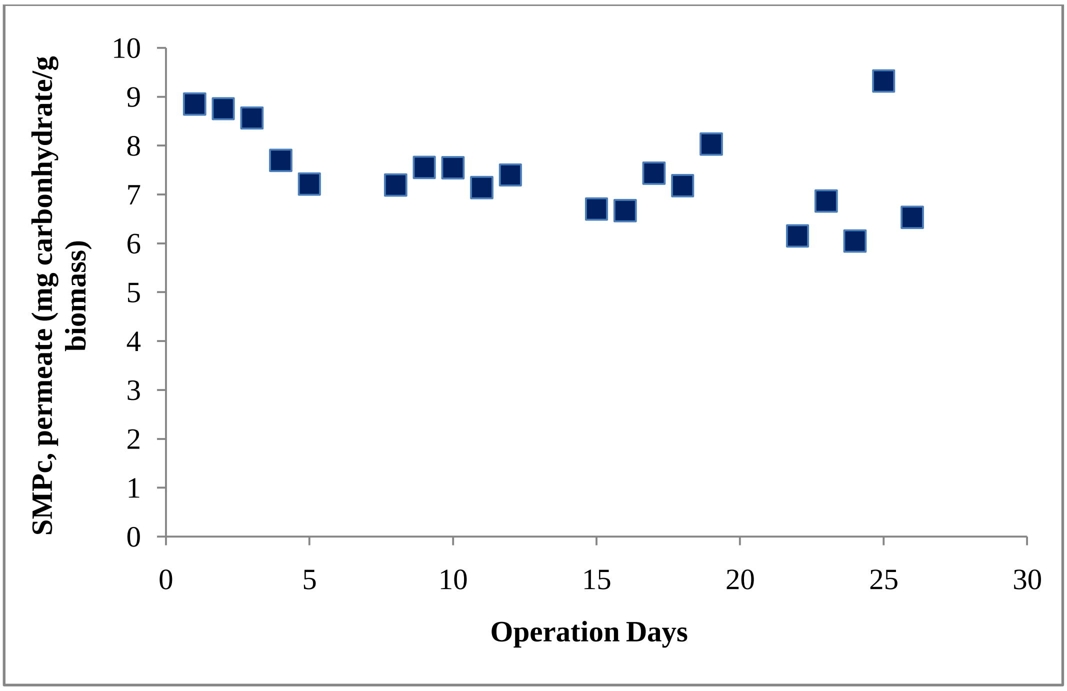



(b)

**Figure 4.27 :** The graphs of SMPactive sludge analysis during second period. (a) SMPp, active sludge (mg protein/gr biomass) (b) SMPc, active sludge (mg carbohydrate/gr biomass).



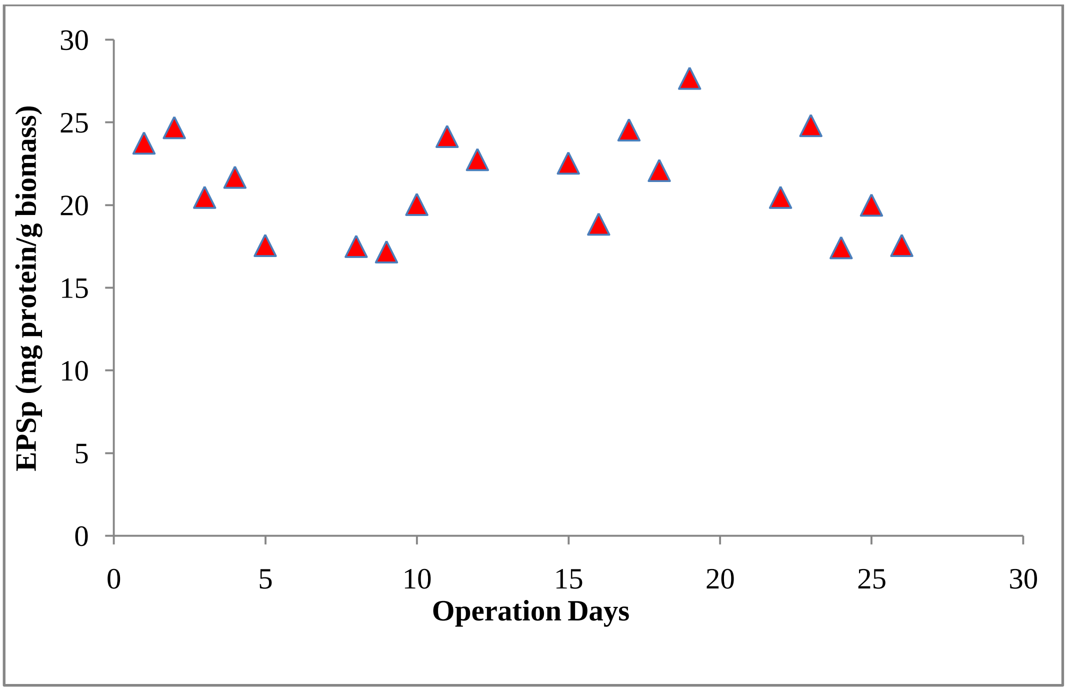

(c)



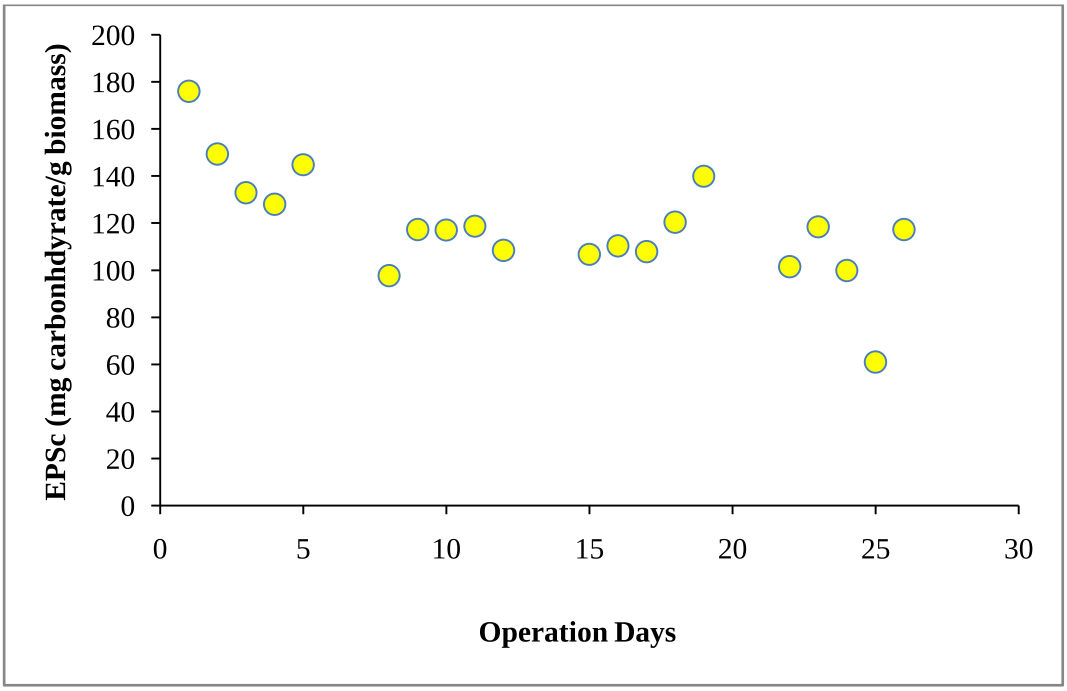

(d)

**Figure 4.27 (continued) :**The graphs of $SMP_{permeate}$ analysis during second period. (c) $SMP_{p,\ permeate}$ (mg protein/gr biomass) (d) $SMP_{c,\ permeate}$ (mg carbohydrate/gr biomass).

The graphs of EPS analysis are given in Figure 4. 28 (a,b). As it is seen from graph (a), there was not a dramatic increase and decrease in the rate of $EPS_p$ concentrations. As it is seen from graph (b), a remarkable decrease was observed in the $EPS_c$ concentration and according to average values, average $EPS_p$ concentration was lower than that of first period but average $EPS_c$ concentration was higher than that of first period.




(a)




(b)

**Figure 4.28 :** The graphs of EPS analysis during second period. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

The activated sludge filtration performance of AgNP-PES composite membrane is given at Figure 4. 29. As it is seen from graph, a less decrease was observed compared with filtration performance of bare PES membran. In this period, $J_{ss}$ that is average permeate flux of the last five day was 11 L/m$^2$*h. Compared with $J_{ss}$ of first period, $J_{ss}$ of second period had higher permeate flux owing to preventing membrane biofouling of silver nanoparticle.According to literature, for instance, compared with bare polysulfone (PS) membranes, AgNP incorporated PS membranes (with less than 1% wt nanosilver) could significantly reduce biofouling (Koseoglu-Imer et al. 2012). Thus, nanosilver is used in membranecoatingorsurfacemodificationforpreventingmembranebiofouling (Kim and Vander Bruggen 2010, Rana andMatsuura 2010).As mentionedbefore, nanosilver has strongantimicrobialactivitiestoinhibitbacterialgrowthandbiofilmformation(Choi et al. 2010) on thesurface of a membrane.

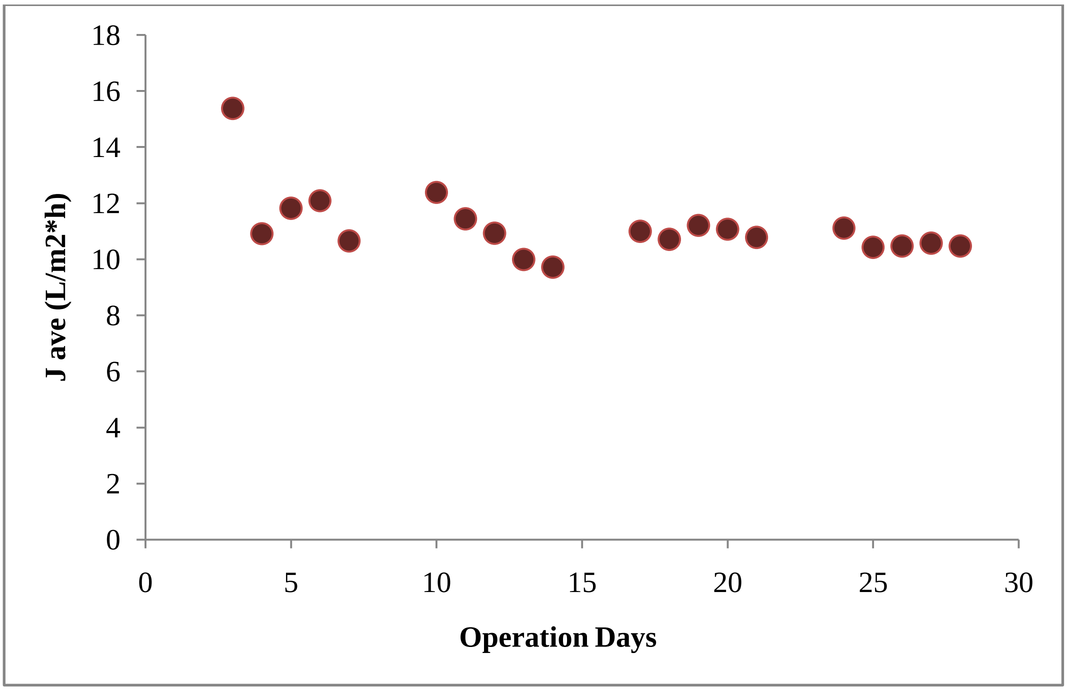



**Figure 4.29 :** The activated sludge filtration performance of AgNP-PES composite membrane during second period.

The graph of COD analysis is given in Figure 4. 30. As it is seen graph, a decreasing trend was observed in the COD removal efficiency over time and average of COD removal efficiency was 88 % in this period. Compared with COD removal efficiency of first period, in the second period COD removal efficiency was lower. Namely, heterotrophic bacteriacould not consume biodegradable substrate. It means that released $Ag^+$ from AgNP-PES composite membrane had a negative impact on bacterial activity. However, autotrophic bacteriacontinued to remove organic nitrojen and ammonia although slow-growing bacteria that was nitrosomonas and nitrobacter was resposible for TKN removal.

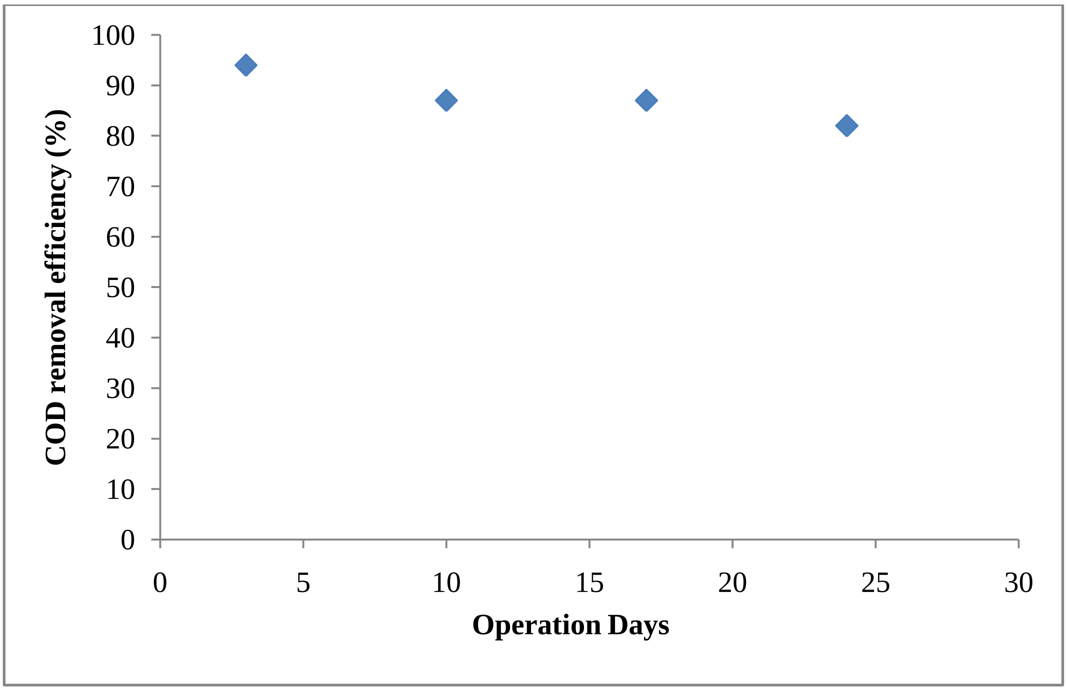



**Figure 4.30 :** The graph of COD efficiency during second  period.

The graph of TKN and TP analysis is given in Figure 4. 31 and 4.32. Effluent TKN concentration of permeate was higher than first period and TP values were shown an incerase that was from 40 to 70 mg/L  over time according to first period**.**

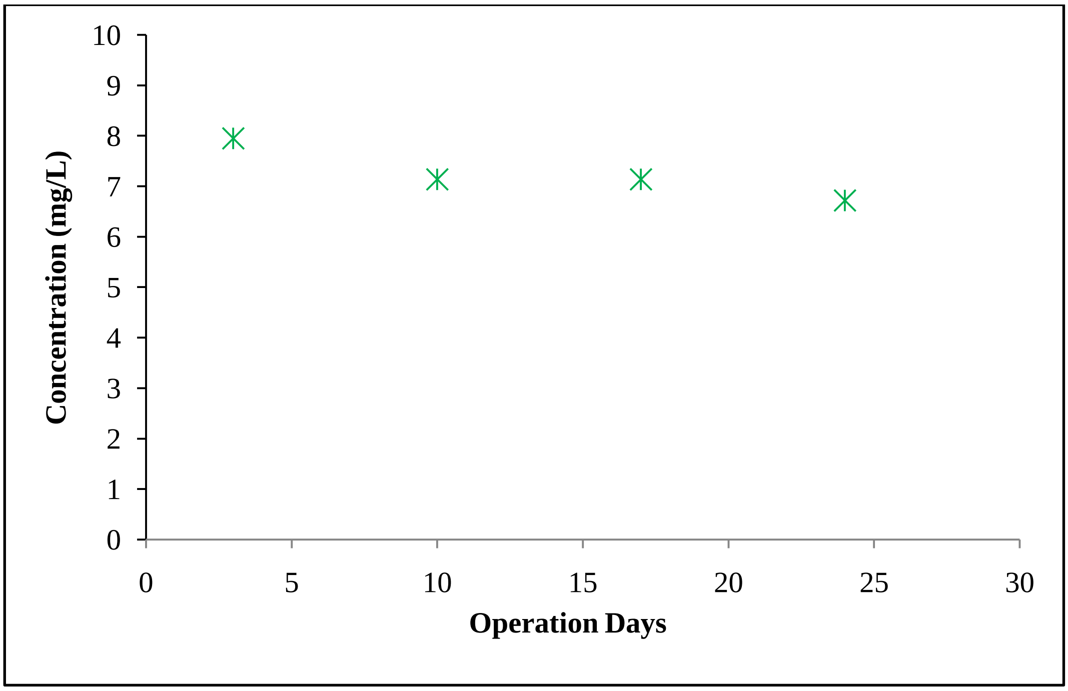



**Figure 4.31 :** The graph of TKN concentrations during second period.

However, TP value had a decrease  that was from 75 to 65 mg/L in the first period. Also, the maximum and minimum value of TP was 75 and 40 mg/L in the first period. Moreover, these maximum and minimum values was the same in the second period.

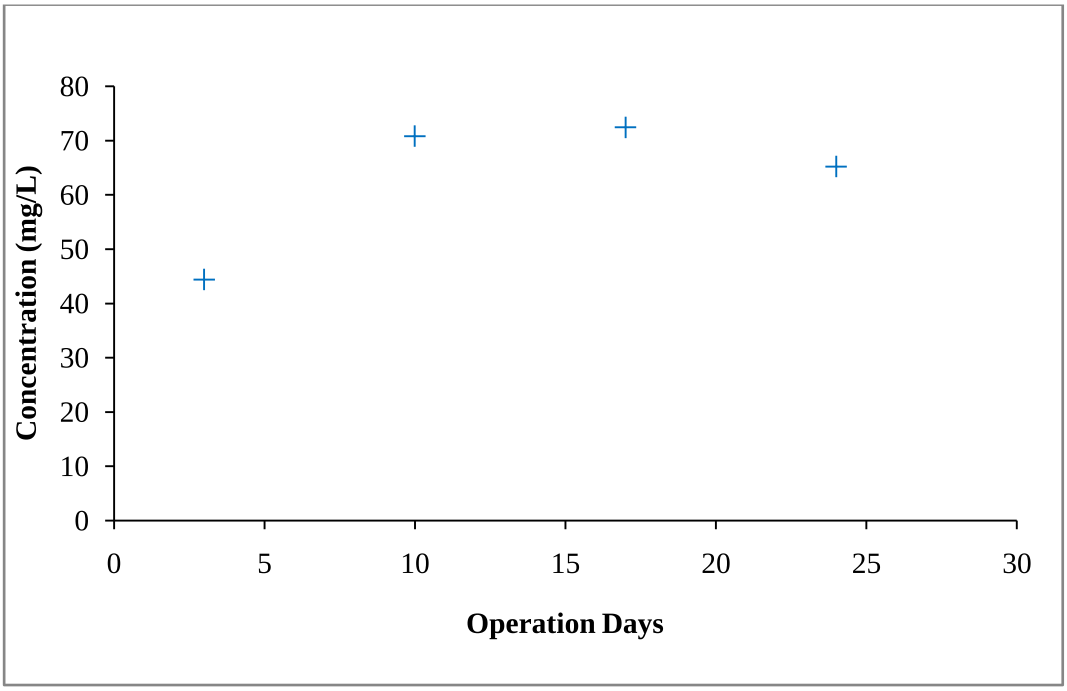



**Figure 4.32 :** The graph of TP concentrations during second period.

According to Dolette et al., during the activated sludge process, organic nitrogenand phosphorus are removed by various microbialcommunities. Several studies have investigated the impactof AgNPs on nitrification and the effects onmicrobial populations that perform these processes. However, results from nitrification studies are divergent with no inhibition and varying degrees ofinhibition  observed on nitrification followingAgNP addition in WWTPs or bioreactors at concentrationsbetween 0.4 and 1 mg Ag $L^{-1}$.

The observed variation is most likely explained by thedifferences in input variables. A number of parametersdiffer between studies, all of which are known to influenceAgNP fate and toxicity e.g. intrinsic AgNP properties(size, coating), Ag concentration, sludge/wastewater properties(temperature, ionic strength (IS)), total suspendedsolids (TSS) and dissolved organic carbon, (DOC)), thetype of sludge/wastewater used (realistic or artificial)and general experimental set-up (e.g. light intensity andwavelength which may cause photocatalytic reductionof Ag+ and AgNP).

### 4.2.3 Third period: Bare PES membrane& addition of suspended silver nanoparticle test results

The graph of MLSS is given in Figure 4. 33. As it is seen from graph, MLSS concentration was observed in the range of 4380-5260 mg/L. MLSS concentration did not changed remarkably in the third period similar to second period. The MLSS concentration of activated sludge taken from MBR were averagely found as4859 mg/L. This concentration was lower than MLSS of second period. Although AgNP was added to activated sludge of membrane bioreactor, it did not affect biomass adversely .

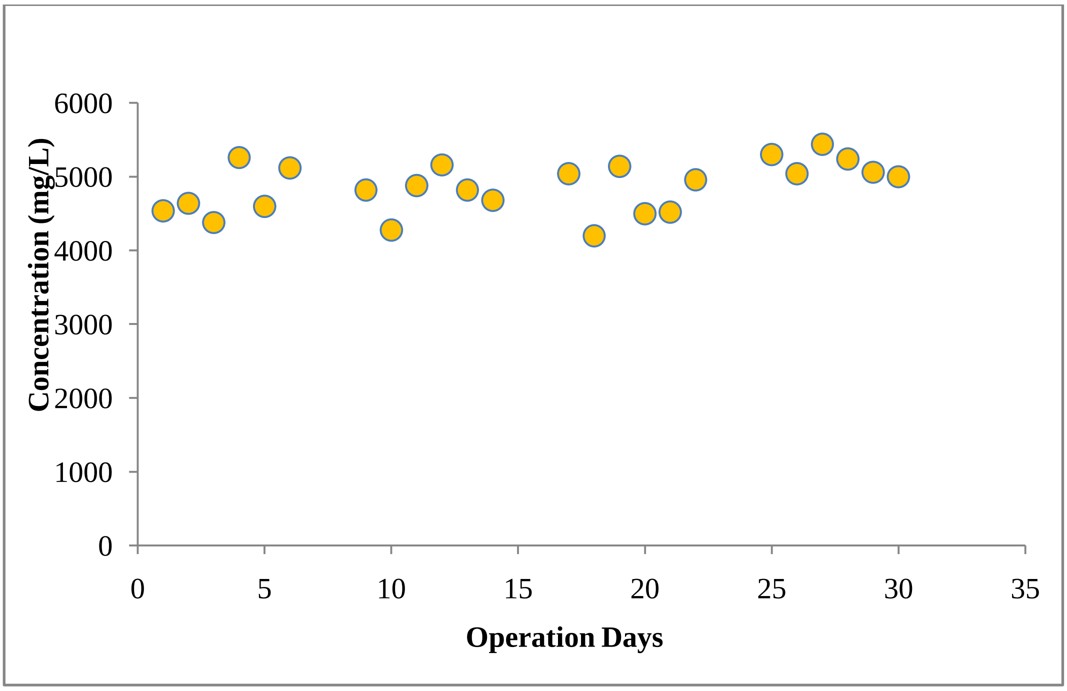



**Figure 4.33 :** The MLSS concentration values during third period.

The graphs of $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$ are given in Figure 4. 34. As it is seen from graph (a), the graph of $OD_{sludge}$ was observed the same as graph of MLSS concentration. However, OD value of activated sludge was lower than other two periods. As it is seen from $OD_{supernatant}$ graph, $OD_{supernatant}$ had a slight increase in the third period. This situation showed a change in the the settling properties of the sludge but it is negative change. As it is seen from $OD_{permeate}$ graph, the samples of OD taken from the permeate of the MBR values were averagely found as0.001 mg/L. This value was lower than those of first and second period. OD values of permeate were 0,002 and 0,003 in the first and second period, respectively.

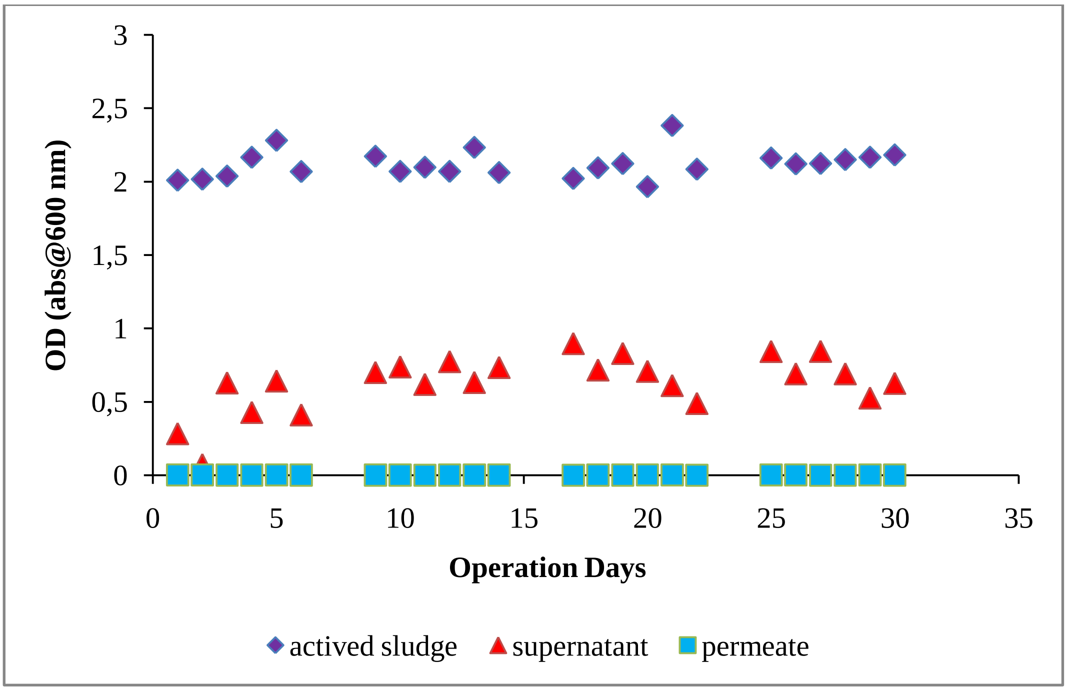
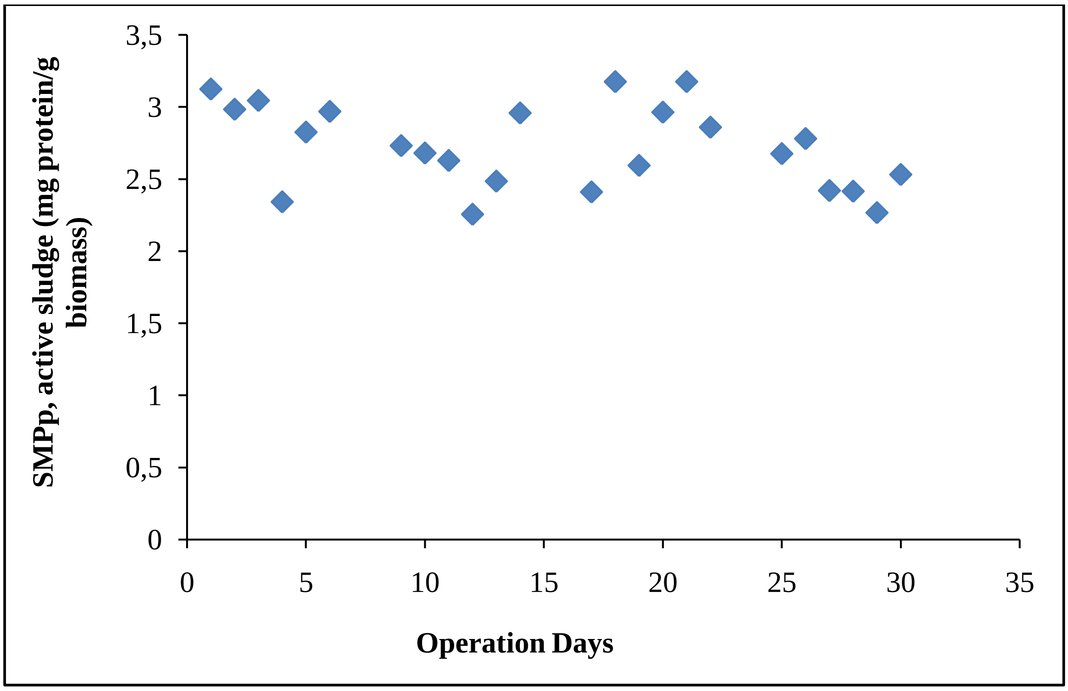
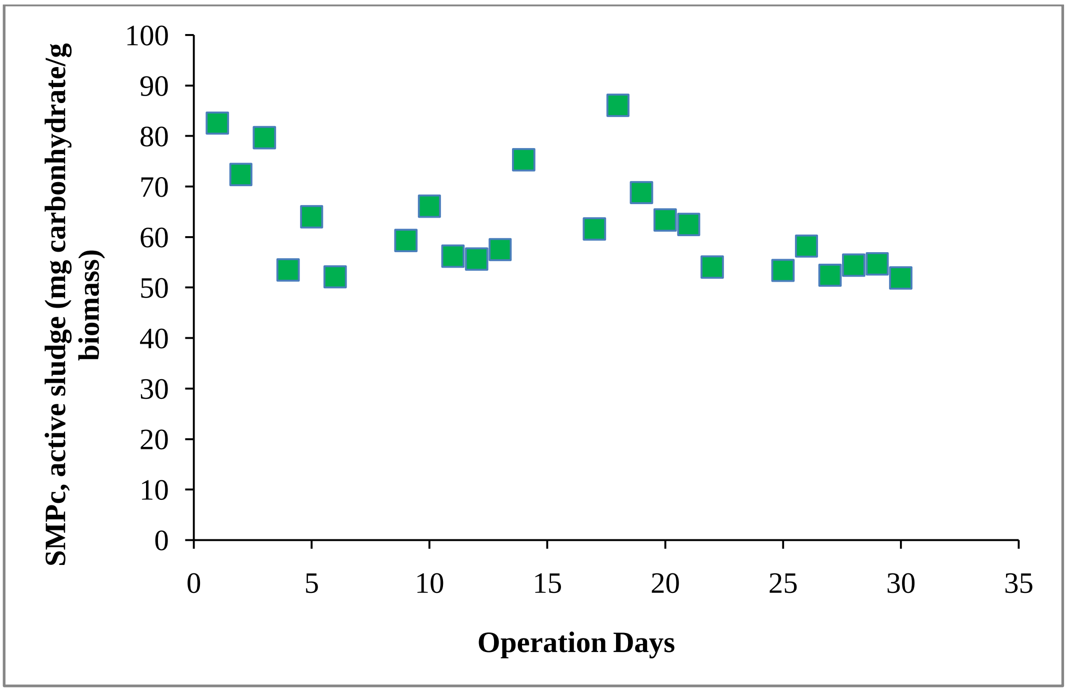



**Figure 4.34 :** $OD_{sludge}$, $OD_{supernatant}$, $OD_{permeate}$ values during third period.

The graphs of SMP analysis are given in Figure 4. 35 (a-d). As it is seen from graph 4.35 (a), the $SMP_p$ concentration of actived sludge changed in the range of 3-2.5 mg/gr VSS. Namely, there was not a dramatic increase and decrease in the $SMP_p$ concentration of actived sludge. As it is seen from graph 4.35 (b), a decrease was observed in the $SMP_c$ concentration of actived sludge. Also, according to average values, it was observed that $SMP_{p,\ activated\ sludge}$ and $SMP_{c,\ activated\ sludge}$ concentration had lower values compared with first period and second period.As it is seen from graph 4.35 (c), a decrease was observed in the SMPp, permeate concentration over time. Averagely, protein concentration of $SMP_{permeate}$ had 2 mg protein/gr biomass value this values was 4 mg protein/gr biomass values in this period but in the first and second period. As it is seen from graph 4.35 (d), the carbonhydrate concentration of SMPpermeate did not has noticable change. According to average values, average SMPp, permeate concentration was lower than average SMPp, activated sludge. Average SMPc, permeate concentration was the same average SMPc, activated sludge concentration as. It means that membrane could keep carbonhydrate in ths period. Also, protein could keep in this period so protein concentration of permeate was lower than that of activated sludge of membrane bioreactor. Compared with average values of the other period, average SMPp, permeate and SMPc, permeate concentrations of third period was lower values than first and second periods. The reason might that AgNP was used as suspended. Hence, produced bacterial products by bacteria was affected negatively.

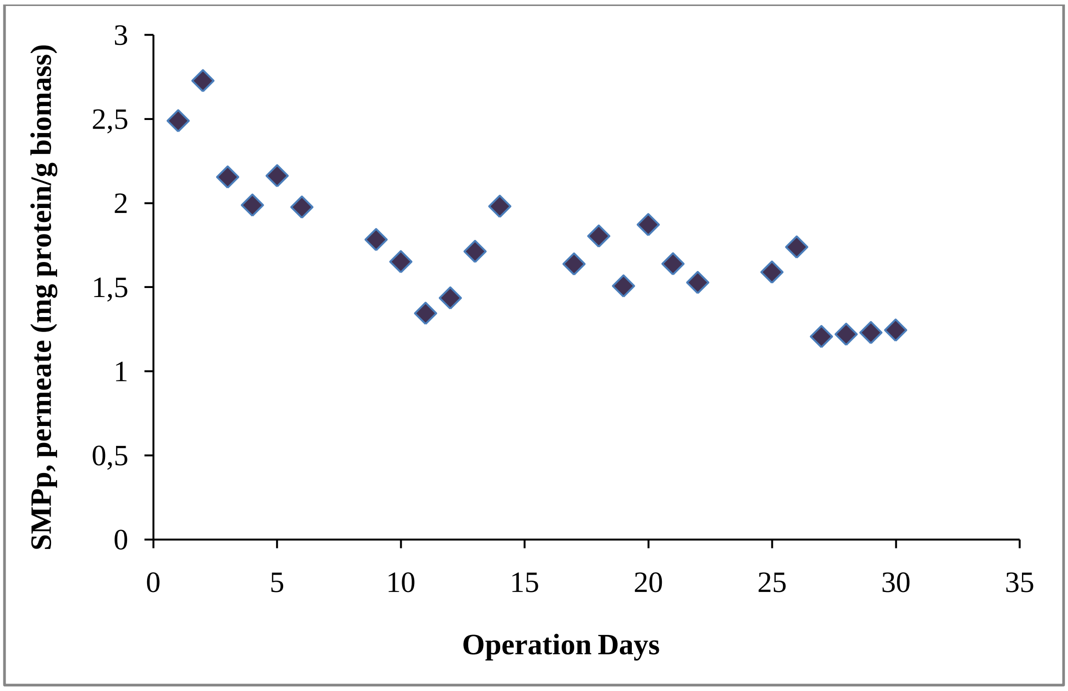



(a)

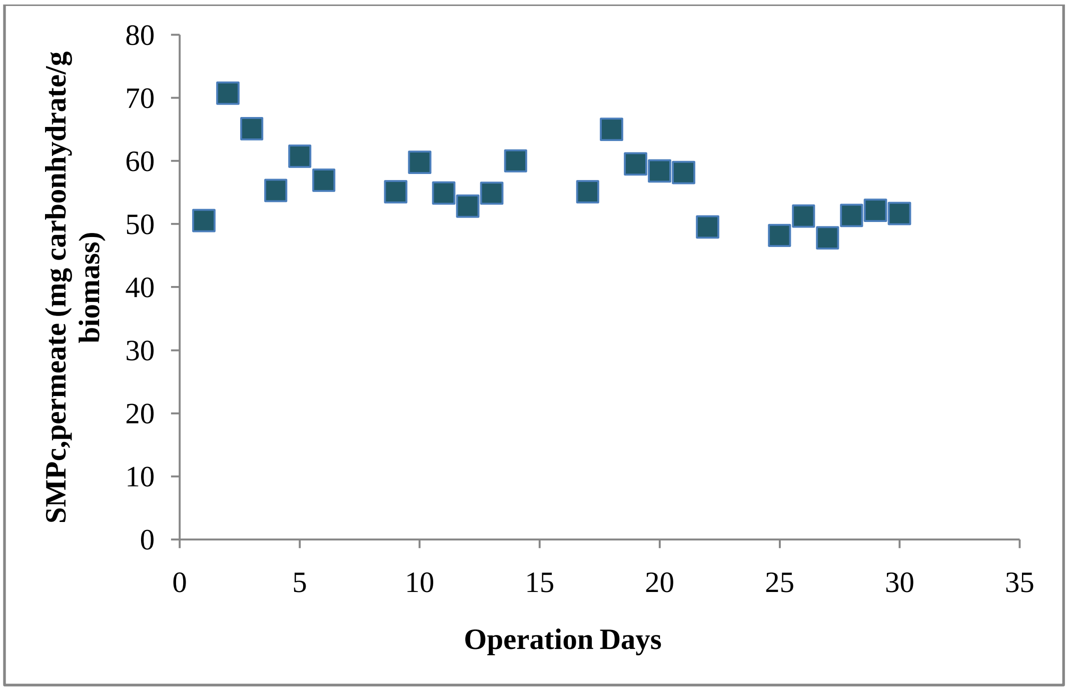



(b)

**Figure 4.35 :** The graphs of $SMP_{active\ sludge}$ analysis during third period. (a) $SMP_{p,\ active\ sludge}$ (mg protein/gr biomass) (b) $SMP_{c,\ active\ sludge}$ (mg carbohydrate/gr biomass).



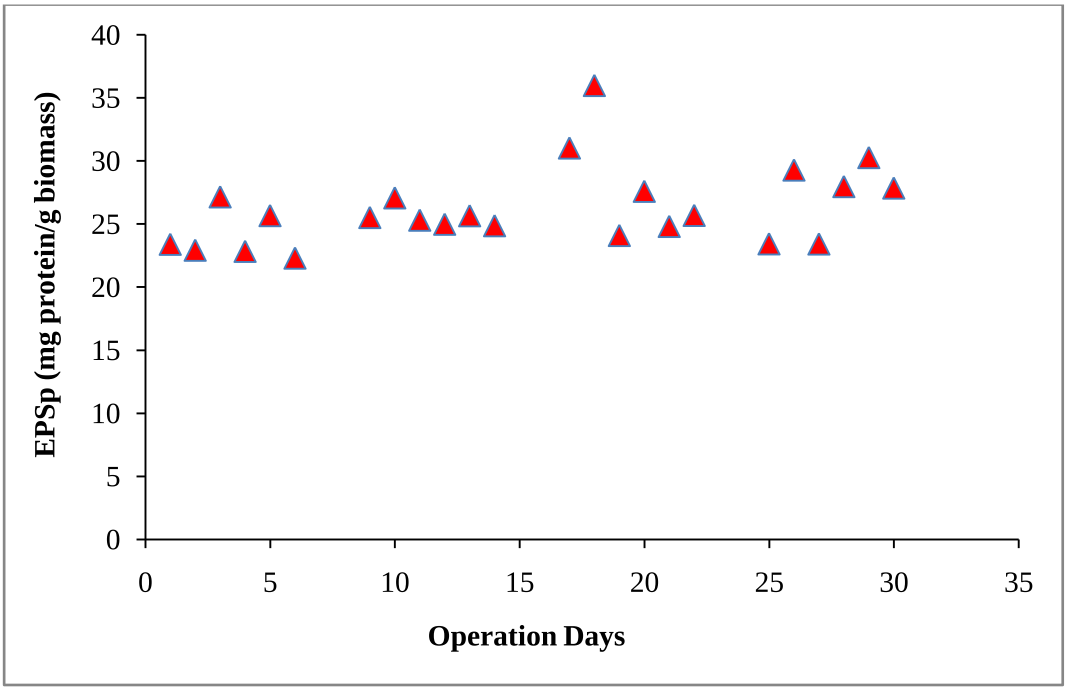

(c)



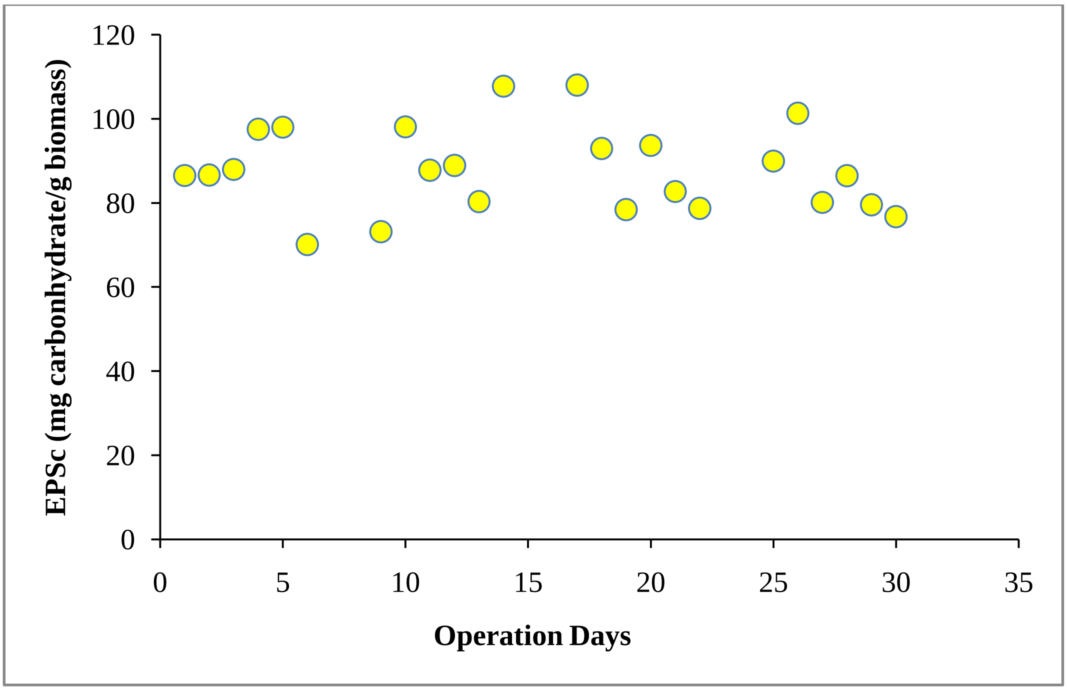

(d)

**Figure 4.35 (continued) :**The graphs of $SMP_{permeate}$ analysis during third period. (c) $SMP_{p,\ permeate}$ (mg protein/gr biomass) (d) $SMP_{c,\ permeate}$ (mg carbohydrate/gr biomass).

The graphs of EPS analysis are given in Figure 4. 36 (a,b). As it is seen from graph (a) and (b), there was not a dramatic increase and decrease in the rate of $EPS_p$ concentrations. According to average values, average $EPS_p$ concentration was higher than that of second but it was lower than average $EPS_p$ concentration of first period and average $EPS_c$ concentration was lower values than first and second periods.




(a)




(b)

**Figure 4.36 :** The graphs of EPS analysis during third period. (a) $EPS_p$ (mg protein/gr biomass) (b) $EPS_c$ (mg carbohydrate/gr biomass).

The activated sludge filtration performance of AgNP-PES composite membrane is given at Figure 4. 37. As it is seen from graph, much more decrease was observed compared with filtration performance of AgNP-PES composite membrane. In this period, $J_{ss}$ that is average permeate flux of the last five day was 5 L/$m^2$*h.

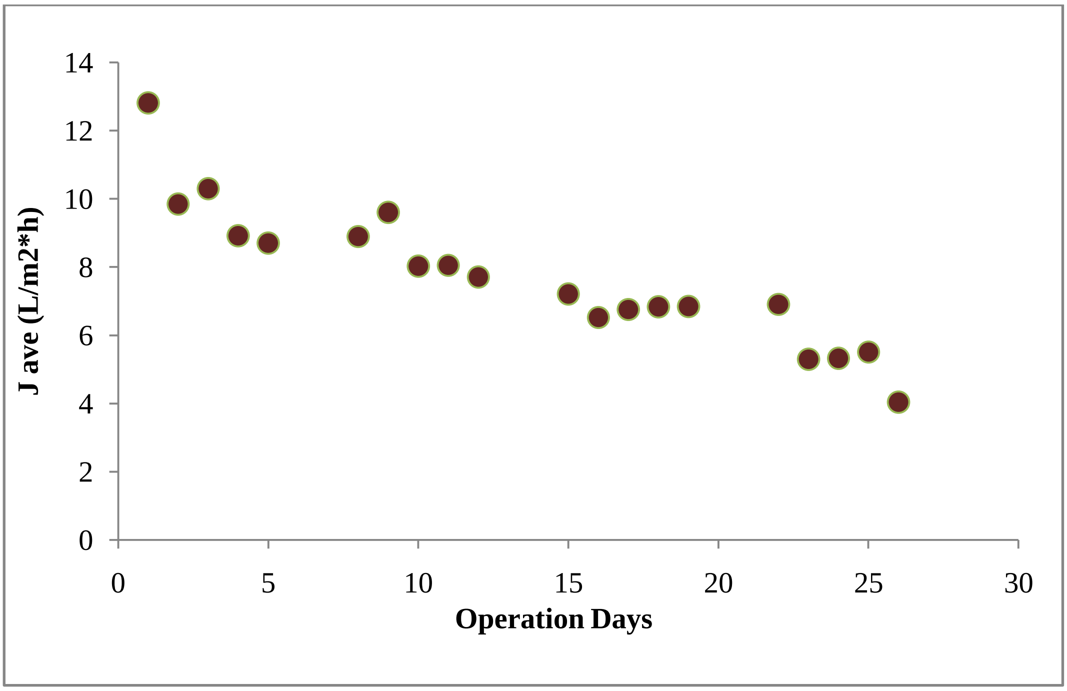



**Figure 4.37 :** The activated sludge filtration performance of bare PES membrane during third period.

The graph of COD analysis is given in Figure 4. 38. As it is seen graph, a increasing trend was observed in the COD removal efficiency over time and average of COD removal efficiency was 92 % in this period.

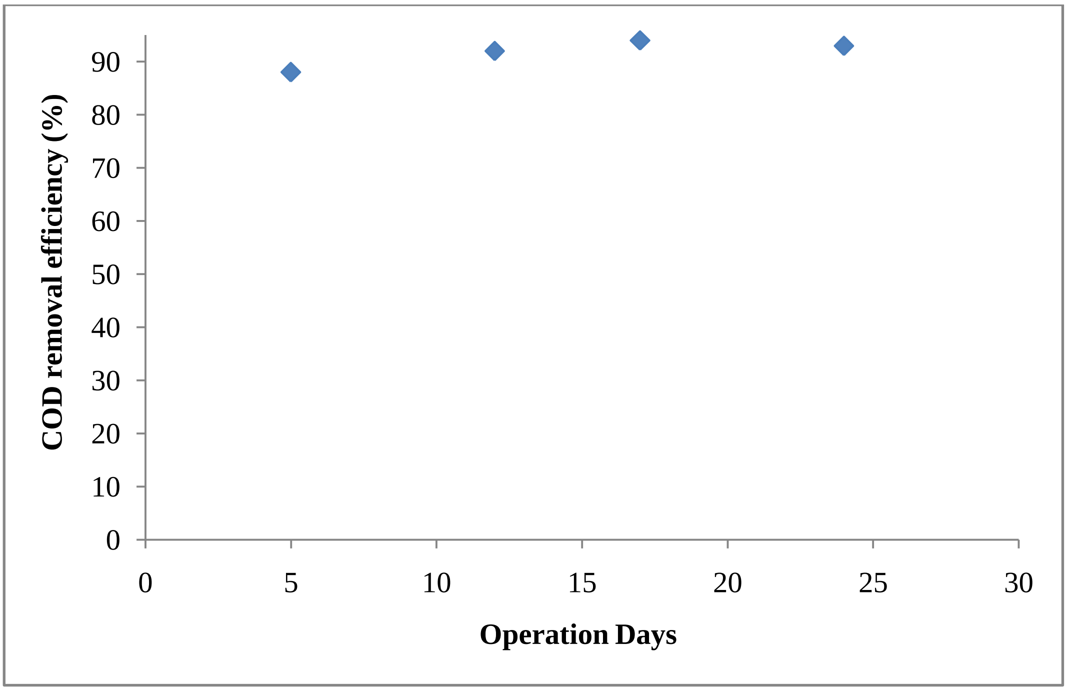



**Figure 4.38 :** . The graph of COD removal efficiency during third period.

The graph of TKN and TP analysis is given in Figure 4. 39 and 4.40. Effluent TKN concentration of permeate was lower than those of the other periods and TP values were showed an incerase over time but its values was lower.

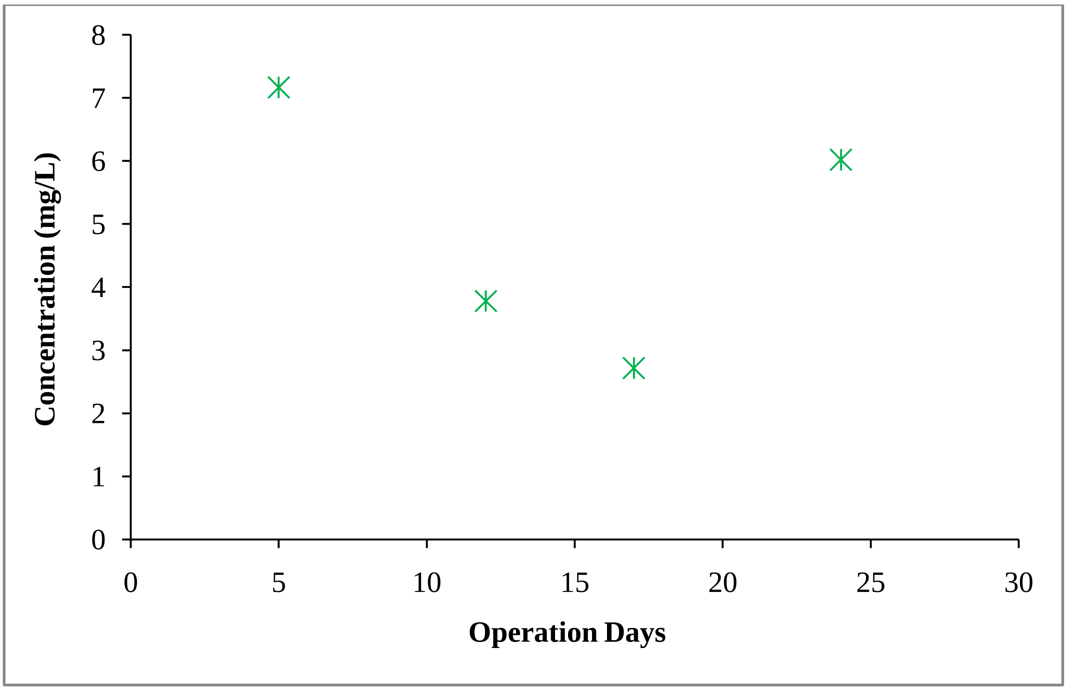



**Figure 4.39 :** The graph of TKN concentrations during third period.

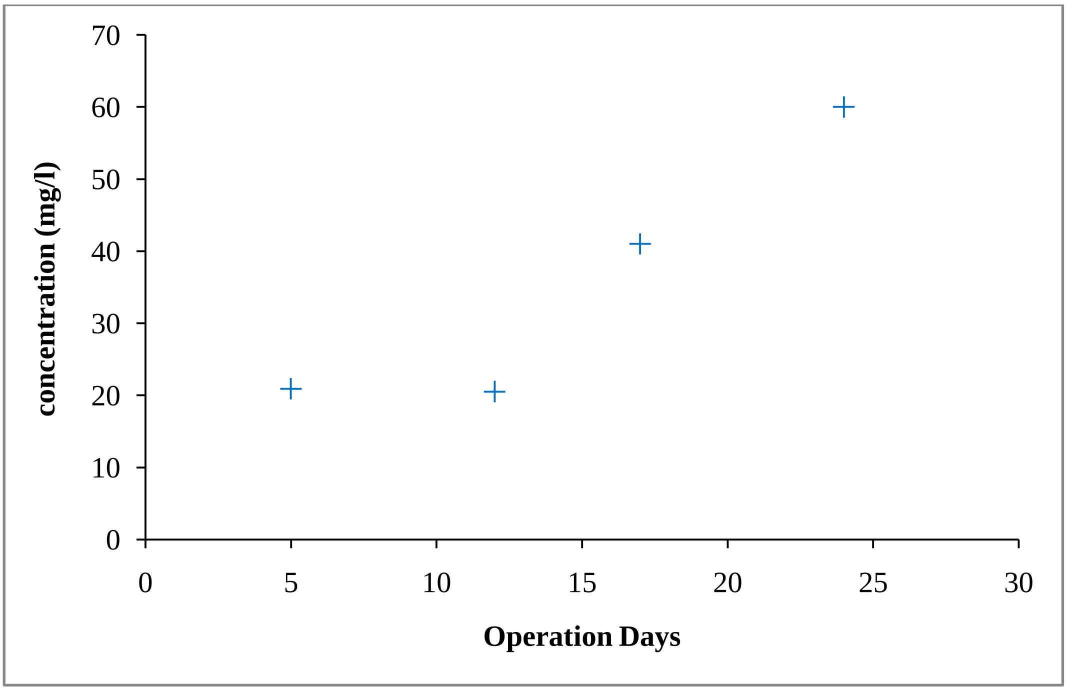



**Figure 4.40 :** The graph of TP concentrations during third period.

# 5. CONCLUSIONS

Results of experiments conducted in this thesis study can be classified into two major categories as results of short-term and long-term experiments.

- The results of short-term experiments:

The results of short-term experiments can be analyzed in two subgroups.

1. The results of different exposure times at constant concentration experiments

Generally, silver nanoparticle exposure had an positive impact on filtration performance and a negative impact on bacterial products. Positive impact on filtration performance means that high permeate flux value obtained. In other words, high flux value can obtain by reducing the membrane fouling problem. Hence, the best appropriate exposure time try to find. Positive effect of AgNP exposure on filtration performance was observed but while exposure times increased, filtration performance of bare PES membrane showed decrease. On the other hand, negative effect of AgNP exposure on bacterial products was observed but while exposure times increased, bacterial products showed increase. That is to say, microorganisms showed resistance to toxic effects of AgNP exposure in time.

2. The results of different concentration at constant exposure times experiments

In the second stage of short-term experiment (at the same exposure time and the changing concentration), decrease AgNP concentrations caused filtration performace to decrease but caused bacterial products to increase.

- The results of long-term experiments:

The membrane fouling can be attributed to both membrane pore plugging and sludge cake deposition on membranes. Although the factors affecting membrane fouling is so various, many researchers suggest that soluble microbial product (SMP) and extracellular polymeric substances (EPS) secreted by bacteria also play important roles in the formation of sludge cake on membrane surfaces. Thus, the membrane fouling problem or low mebrane filtration performace is proportional high bacterial product amounts (SMP, EPS). However, according to study of Zhang et al., (2013) the long-term silver exposure did not change the membrane fouling rate although EPS concentration increased significantly. Therefore, EPS and SMP can be one of the factors affecting membrane fouling but they have not sole responsibility for it.

As it is known, AgNP incorporated membranes have been commonly using due to reducing fouling problems. Because nanosilver has strong antimicrobial activities to inhibit bacterial growth and sludge cake formation on the surface of the membrane. Thus, AgNP-PES composite membrane was used in the second period and although filtration performance showed increase in comparison with bare PES, generally it did not observed a remarkably decrease in the amounts of bacterial products. However, used AgNP form in the second period is blended. Released silver ions ($Ag^+$)should take into consideration because $Ag^+$ has antimicrobial property like AgNP and released $Ag^+$ to mixed liquor of the MBR may have impact on microbial activity adversely. Concordantly, it was observed that COD removal efficiency had a decrease in this period. Thus, as mentioned in the purpose of the study, effects of this possible releases on filtration performance, bacterial products and wastewater treatment performance was aimed to investigate by comparing effects of silver nanoparticle which added to mixed liquor of the MBR. Thus, 10 mg AgNP/L was added to mixed liquor of the MBR daily in the third period. According to results of this period, MLSS, bacterial products was lower than second period. Nonetheles, though bacterial products was low, filtration performance was not high. What's more, COD removal efficiency showed increase compareted with second period interestingly. According to study of Zhang et al., (2013) effluent water quality was not affected by the long-term nanosilver loading but they used influent AgNP concentration of 0,10 mg /L and it is conclude that COD removal efficieny did not change. Also, this results was associated with activated sludge can effectively reduce nanosilver toxicity by adsorbing or precipitating AgNPs and silver ions (Ag+) released from the dissolution of AgNPs. Average Values of Experiments Results for Three Periods During MBR Operation is given Table 5.1.

**Table 5.1 :** Average Values of Experiments Results for Three Periods During MBR Operation.

| Parameter | Bare PES membrane | AgNP-PES nanocomposite membrane | Bare PES membrane & addition of 10 mg AgNP/L |
|---|---|---|---|
| MLSS(mg/L) | 4702 | 4990 | 4859 |
| $OD_{permeate}$ | 0.002 | 0.003 | 0.001 |
| SMPp, activated sludge (mg protein/g biomass) | 6 | 4 | 3 |
| SMPp, permeate (mg protein/g biomass) | 4 | 4 | 2 |
| SMPc, activated sludge (mg carbonhydrate/g biomass) | 80 | 80 | 60 |
| SMPc, permeate (mg carbonhydrate/g biomass) | 80 | 70 | 60 |
| EPSp (mg protein/g biomass) | 30 | 20 | 26 |
| EPSc (mg carbonhydrate/g biomass) | 110 | 120 | 90 |
| $J_{ss}(L/m^2*h)$ | 7 | 11 | 5 |
| COD removal efficiency (%) | 96 | 88 | 92 |

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