Journal of Environmental Health and Sustainable Development

Studying the Efficiency of XAD-7HP Anionic Resin in the Extraction of Humic Acid from Surface Water

Hassan Hashemi [1], **Mahdi Safari** [2*]

[1] Research Center for Health Sciences, Institute of Health, Department of Environmental Health Engineering, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran.
[2] Department of Environmental Health Engineering, School of Health, Kordestan University of Medical Sciences, Sanandaj, Iran.

ARTICLE INFO

ORIGINAL ARTICLE

Article History:
Received: 12 March 2017
Accepted: 10 July 2017

***Corresponding Author:**
Mahdi Safari

Email:
safari.m.eng@gmail.com

Tel:
+989188128262

Keywords:
Humic Substances,
XAD-7HP,
Raw Water

ABSTRACT

Introduction: Humic substances (HSs) are very complex and heterogeneous organic matter with high molecular weight and various functional groups, which are produced from the chemical and biological degradation of plants and animal tissues. HS can cause: colour, odour and taste problems in drinking water, biological growth in distribution systems, increase in chlorine demand for disinfection, membrane fouling and especially, formation of disinfection by-products (DBPs) after disinfection process. The aim of this study is to determine the effectiveness of XAD-7HP resin in the extraction of humic substances from raw water.

Materials and Methods: In the extraction of humic substances from water samples, amberlit anionic XAD-7HP resin with a strong cationic resin AG MP50 was used, while for the determination of humic acid, a High Performance Liquid Chromatography (HPLC) system equipped to BIO SUIT SEC columns was used.

Results: The average extraction efficiency for XAD-7HP was 77% and HA concentration determined in all seasons ranges from 0.15 to 0.29 mg/L in raw water.

Conclusions: From the findings of this study, it can be concluded that the use of XAD-7HP is a proper and effective method for the extraction of HS and its extraction efficiency is more influenced by pH and turbidity than other parameters. It can also be deduced from this study that XAD-7HP resin was most efficient at a pH of 2 and an increase in turbidity resulted in a corresponding decrease in the efficiency of resin.

Citation: Hashemi H, Safari M. **Studying the Efficiency of XAD-7HP Anionic Resin in the Extraction of Humic Acid from surface Water**. J Environ Health Sustain Dev. 2017; 2(3): 363-70.

Introduction

Humic materials are uneven mixtures from organic compounds that are derived from plants, animals, live and dead microorganisms including their products which enter into water by degradation. However, providing a definite definition is difficult for them. Generally organic materials refer to the general classification of chemical materials usually composed of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) [1, 2]. Humic materials have been commonly said to be the most popular organic pollutant in natural raw water with various degradative effects on drinking water, including color change, organic load, and biological degradation in water distribution networks [3]. Humic materials are shapeless, acidic, mostly aromatic, and hydrophobic complexes. They are anionic poly-electric materials ranging from low to medium molecular weights [4]. They are also in macro-molecular form with negative load in pH of natural water due to the presence of functional groups. Carboxylic, hydroxyl phenolic, and hydroxyl-calcium are the most important functional groups; however, their negative load is mainly due to the presence of carboxyl and phenolic groups in the first step. The chemical compounds of humic materials depends on the type of functional group as they are in different weight percentage in ranges of 40-60% carbon, 30-50% oxygen, 3-6% hydrogen, and 1-4% nitrogen[5, 6]. The presence of humic materials in water resources based on the solubility in acid or alkaline are usually classified into two main groups namely; humic acid (HA) and folic acid (FA) groups. HA is soluble in weak alkaline environment, but precipitates after being acidic, while FA is soluble in low pH.

There are various technique to separate and concentrate natural organic materials (NOM) in aqueous environments. These include, surface absorbance of resin (usually XAD resins), ultrafiltration, reverse osmosis (RO), low temperature evaporation (40-50°C), and other techniques. Combined techniques are also used in some studies [7, 8]. Most developed and applied techniques to separate humic materials in aqueous environments are based on amberlite XAD resins, acrylic ester, and styrene deionylbenzene resins; meanwhile XAD, XAD-2, and XAD-8 are mostly applied to separate humic materials in aqueous environment [9]. Another technique in the separation of humic materials based on anionic exchangers is the use of diethylaminoethyl (DEAE) cellulose [10]. The most common technique used to separate natural organic materials in surface water is adsorption using resin with big anionic pores, particularly the use of XAD-8 by Aiken[11]. XAD technique was used by International Association of Humic Materials for standard separation of humic materials in aqueous environments, and XAD-8 resin has been selectively used for standard separation [9]. XAD-8 is an excellent absorbent for humic materials in low pH. This resin may be used to separate humic materials from high amounts of water (10-100 L) [12]. All XAD resins usually absorb organic materials by hydrophobic link. Their precise amount of absorbance has not yet been known [4].

For the presence of various interrupting materials in water to analyze HPLC, it is necessary to extract these materials from water to determine its value with high precision. The aim of this study is to determine the efficiency of XAD-7HP anionic resin in the extraction of humic acid from input raw water samples to Isfahan water treatment plant.

Materials and Methods

Sampling

The required samples for this study were prepared from the raw water of Zayanderud River as input flow of Isfahan water treatment plant. The volume of the samples needed to analyze humic acid levels is 20 L , using high density polyethylene containers (HDPE) and preserved at 4°C before extraction. The glass containers used in this test were placed in 5% nitric acid for 24 h before usage to ensure the absence of organic materials and were placed in an oven for 1 h after washing.

Extraction materials and column

Sodium humic acid (50-60%) and anionic resin XAD-7HP Amberlite were purchased from Sigma-Aldrich Company while other materials such as IR-120 cationic resin, chloride acid, sodium hydroxide, nitric acid etc were purchased from Merck Company.

For the extraction, a plexiglass cylinder column with 3 cm diameter and 50 cm length was filled by anionic resin. In addition, a plexiglass cylinder column with 3 cm diameter and 20 cm length was filled with cationic resin.

Extraction

An anionic amberlite XAD-7HP resin with a strong AG MP50 catalyst resin were used to extract humic materials from water samples. The needed samples were prepared from raw input water to Isfahan water treatment plant. A volume of 20 L of water for each sample was used based on previous studies. The sample was filtered before extraction using a 0.45µ aqueous-organic filter,

[DOR: 20.1001.1.24766267.2017.2.3.8.6]

after which the sample pH arrived at 2 using a strong hydrochloric acid. The acidic sample was passed through XAD - 7HP using pneumatic pump with 5 ml flow rate. XAD - 7HP column was washed using 0.1 M NaOH, and the adsorbed organic materials were separated from column. The alkaline sample was passed through a strong AG MP50 cationic resin. The schematic of extraction is shown in Figure 1.

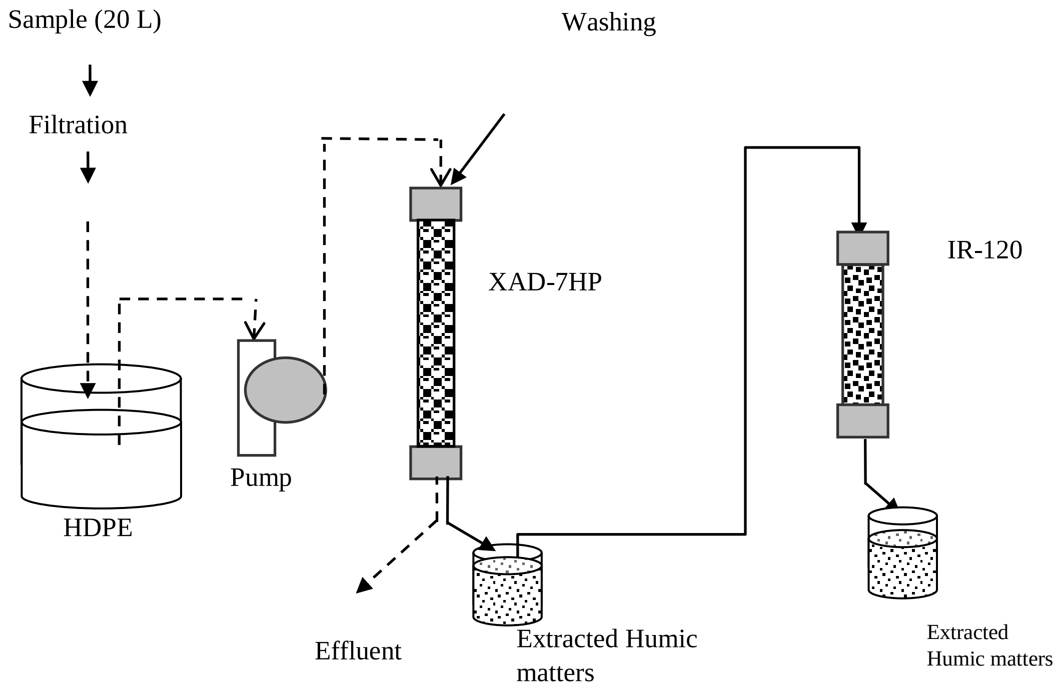

Figure 1: Schematic design of humic materials extraction

Analysis

A high-performance liquid chromatography (HPLC) model 746-HPLC-WATERS equipped with waters 515 HPLC-Pump, Waters 486-UV/VIS detector and manual injector was used. In addition, a column with specifications of BIO SUIT 5 µm HR SEC COLUMN (7.8 × 300 mm) equipped with BIO SUIT GUARD SEC (7.5 × 75 mm) guard was used. Other tests were conducted based on standard techniques of water and wastewater tests. EUTECH pH-meter, model 310 was used to measure pH. In this study, electric conduction was also done using electrometric technique by Digital Hachistic Controller Model HACH Model Sension7.

Data was analyzed based on Pearson correlation statistical test using SPSS software.

Results

The results of this study are shown in Figures 2-6.

[DOR: 20.1001.1.24766267.2017.2.3.8.6]

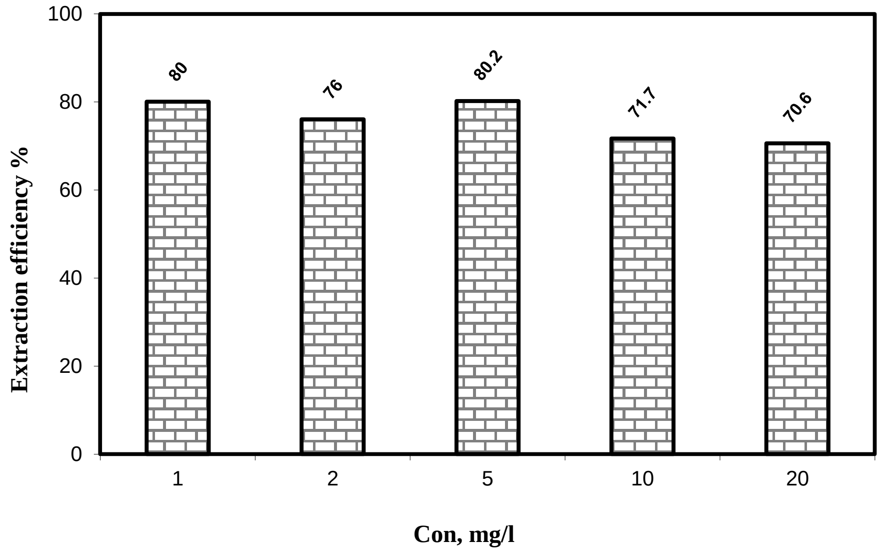

Figure 2: XAD-7HP resin efficiency in various concentrations of humic acid (pH < 2 and constant for all samples)

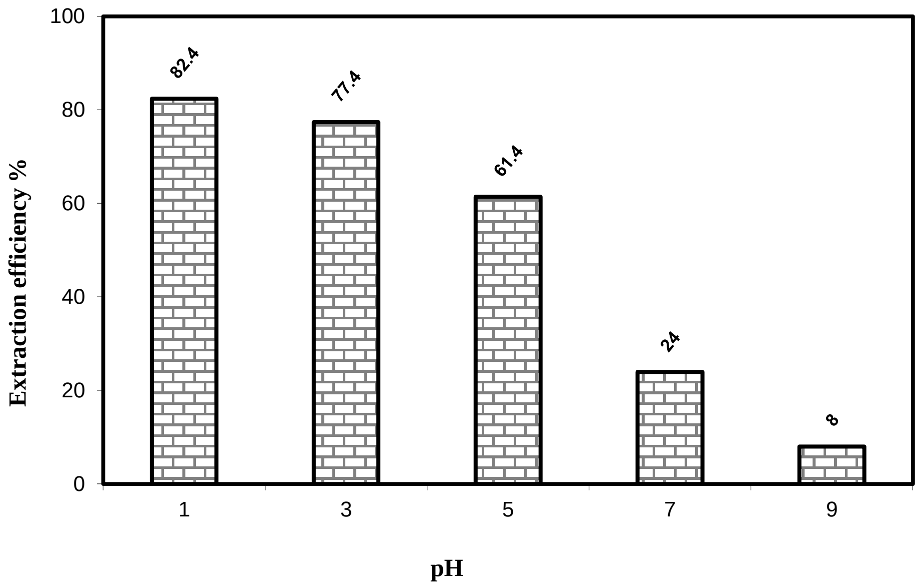

Figure 3: Efficiency of XAD-7HP resin in various pH (humic acid concentration of 5 mg/L and constant for all samples)

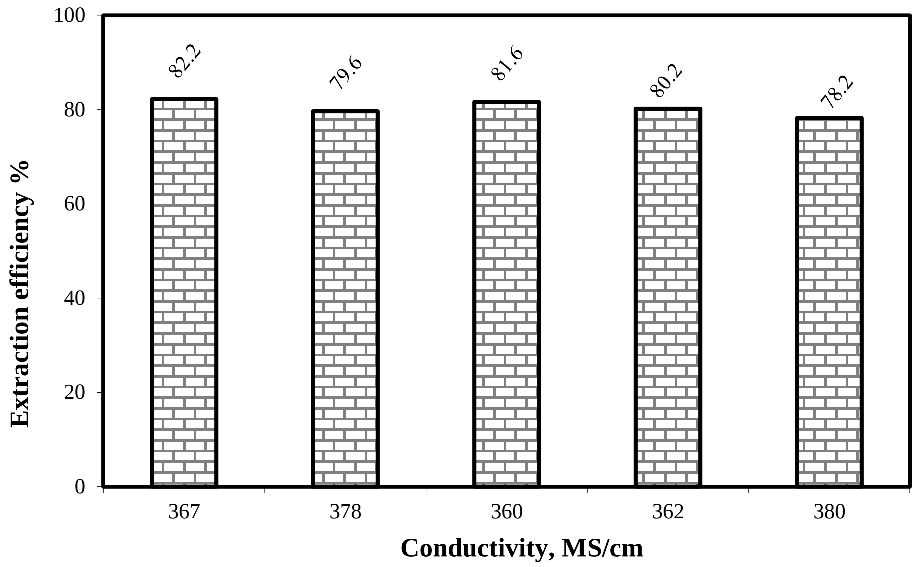

Figure 4: Efficiency of XAD - 7HP resin in various EC (pH < 2 in all samples and concentrations of humic acid is 5 mg/L)

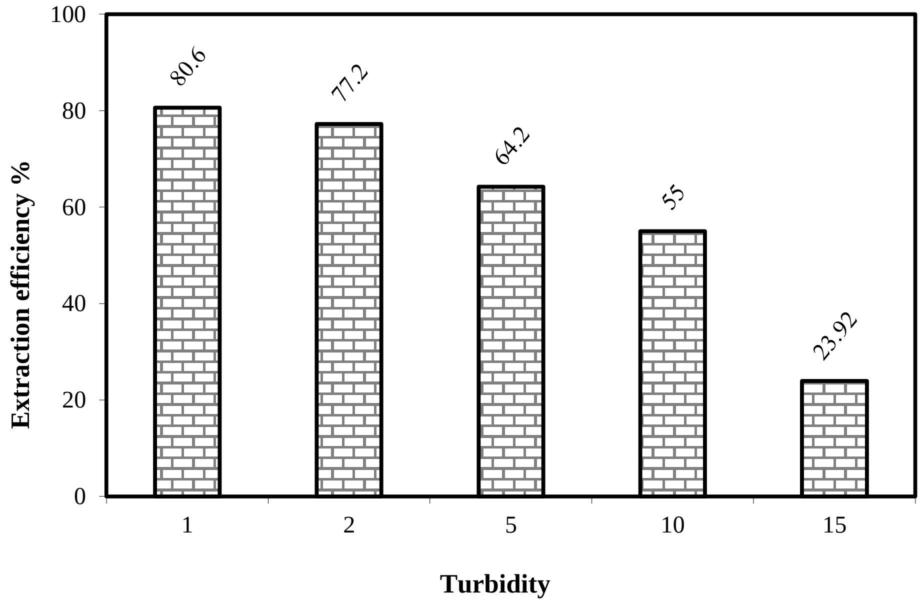

Figure 5: The efficiency of XAD-7HP resin on various turbidities (in all samples pH < 2 and the concentration of humic acid is 5 mg/L)

[DOR: 20.1001.1.24766267.2017.2.3.8.6]

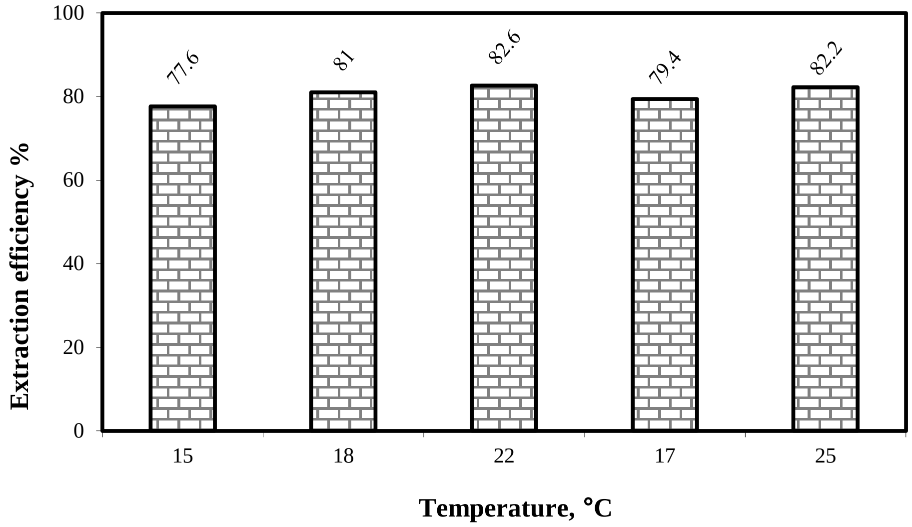

Figure 6: The efficiency of XAD-7HP resin in various temperatures (pH < 2 in all samples and the concentration of humic acid is 5 mg/L)

Discussion

Effect of initial concentration of humic materials in water on efficiency of XAD-8 resin

XAD absorbent resin may use large amounts of water (10-100 L) to separate humic materials [5]. All XAD resins mostly absorb organic materials by hydrophobic link. The precise mechanism of absorbance is still unknown. XAD, XAD-2, and XAD-8 are mostly used to separate humic materials from aqueous environment [13].

The efficiency of XAD resins is influenced by the concentration of humic materials; as though, the higher concentration of these materials leads to the lower performance of the resin. The low extraction of humic materials from XAD resins justifies the interruption of some humic compounds and resin materials, implying that some humic materials have been trapped inside the resin pores. The efficiency of absorbance is actually influenced by the fact that there are some hydrophilic compounds in humic materials that are not adsorbed on resin surfaces [7].

The effect of initial concentration of water on the efficiency of XAD-7HP resin is shown in Figure 2. As observed in this figure, an increase in initial concentration of humic materials reduces the efficiency of XAD-7HP resin, but the Pearson correlation statistical test doesn't show the significant difference between humic materials and resin efficiency (p-value > 0.05).

Effect of water pH on the efficiency of XAD-7HP resin

As earlier mentioned, pH is one of the important parameters on adsorption and extraction of humic materials as it effectively influences the extraction processes.

Figure 3 shows the results related to the effect of pH changes on the efficiency of XAD - 7HP resin. The obtained results show that XAD - 7HP anionic resin has the maximum absorption efficiency in the extraction of humic materials in acidic pH which is observable in all real and standard samples. Pearson correlation statistical test shows the effect of pH changes on the efficiency of XAD-7HP (p-value < 0.05).

Effect of electric conduction (EC) on the efficiency of XAD-7HP resin

EC is a physical property of water that shows the conductivity of electricity. There is a close relationship between EC and total soluble solids (TDS) in water, because anions are the main factor for electricity transfer in solutions and they indicate electrical conductivity.

Changes in EC and the effect of this parameter on the efficiency of XAD-7HP anionic resin is shown in Figure 4. It is observed that increasing

[DOR: 20.1001.1.24766267.2017.2.3.8.6]

EC decreases the efficiency of resin due to increase in TDS probability and as a result, occupancy of resin adsorbent surface by these materials. Although the efficiency of XAD - 7HP resin decreases by increasing EC, Pearson correlation statistical test didn't show any significant relationship between them (p-value > 0.05).

Effect of water sample turbidity on the efficiency of XAD-7HP resin

Turbidity is one of the most serious problems in extracting humic materials from water samples by resins. According to the turbidity of raw water samples, it seems that occupancy of adsorbent resin sites by turbidity agents can be a reason of turbidity effect on reduction of adsorption of the humic materials. In general, increasing turbidity reduces the efficiency of the mentioned anionic resin [14]. As earlier mentioned, the reason for this is adsorbent sites limitation by resin and their occupancy by turbidity. The results related to the effect of turbidity on the efficiency of XAD-7HP anionic resin is shown in Figure 5. It can also be observed that the efficiency of resin is reduced with the increasing turbidity. Pearson correlation statistical test shows that the relationship between turbidity value and the efficiency of XAD - 7HP anionic resin is significant (p-value < 0.05).

The effect of sample temperature on the efficiency of XAD-7HP resin

The seasonal changes of raw water and biological activity influence the quality of input water and its treatment capacity [14]. The NOM amounts might be high during the warmest months of the year which is coincident with the season water is needed at its peak. Therefore, extraction and measurement of humic materials is essential and important. The degradation of aqueous environment consequently results in an increase in organic materials. Also algae and bacterial population increase in high temperatures, resulting in a corresponding increase in biological activities. Thus, an increase in the temperature of water results in a corresponding increase in its humic materials which are compound of various organic materials [15].

The related results to temperature on the efficiency of XAD - 7HP anionic resin is shown in Figure 6. As seen in this figure, resin efficiency decreased with an increase in the temperature of water. This reduction in efficiency can be attributed to the increase in organic load of aqueous environment and also in the biological activity of resin including the occupancy of absorbance sites by biological factors [12]. Although resin efficiency decreases by increasing temperature, Pearson correlation statistical test doesn't show any significant relationship between temperature and efficiency of XAD-7HP resin (p-value > 0.05).

Conclusion

It can be concluded that the use of anionic resins is a proper technique with high efficiency in the extraction of humic materials from aqueous environments. Anionic Amberlite XAD - 7HP resin is a proper resin to extract the humic materials from the raw surface water entrance to the water treatment plant whose efficiency was obtained as 77% in this research. In this study, pH was discovered to be an important and effective parameter in the efficiency of resin, such that the maximum efficiency of resin was obtained at a pH < 2.

Acknowledgements

The authors would like to gratefully acknowledge the Isfahan water treatment plant for their help in the collection of water samples.

Funding

The work was not funded.

Conflict of interest

We affirm that this article is the original work of the authors and have no conflict of interest to declare.

References

1. Amin MM, Safari M, Maleki A, et al. Feasibility of humic substances removal by enhanced coagulation process in surface water. Int J Env Health Eng. 2012; 1:29.
2. Samios S, Lekkas T, Nikolaou A, et al. Structural investigations of aquatic humic substances from different watersheds. Desalination. 2007; 210: 125–37.
3. Maurice PA, Pullin MJ, Cabaniss SE, et al. A comparison of surface water natural organic matter in raw filtered water samples, XAD, and reverse osmosis isolates. Water Res. 2002; 36(9): 2357-71.
4. Lehtonen T, Peuravuori J, Pihlaja K. Characterisation of lake-aquatic humic matter isolated with two different sorbing solid techniques: tetramethylammonium hydroxide treatment and pyrolysis-gas chromatography/ mass spectrometry. Anal Chim Acta. 2000; 424 (1): 91-103.
5. De Wuilloud JC, Wuilloud RG, Sadi BB, et al.Trace humic and fulvic acid determination in natural water by cloud point extraction/ preconcentration using non-ionic and cationic surfactants with FI-UV detection. Analyst. 2003; 128(5): 453-8.
6. Knuutinen J, Virkki L, Mannila P, et al. High-performance liquid chromatographic study of dissolved organic matter in natural waters. 1988; 22(8): 985-90.
7. Susic K, Boto KG. High-performance liquid chromatographic determination of humic acid in environmental samples at the nanogram level using fluorescence detection. J Chromatogr A. 1989; 482(1): 175-87.
8. Mingquan Y, Dongsheng W. Enhanced coagulation in a typical North-China water treatment plant. Water Res. 2006; 40 (19): 3621-7.
9. Perisic M. A new method of drinking water purification for Zrenjanin conforming to the techno-economic and environmental quality standards, Tehnika. 2005; 5: 9-17.
10. Bao-yu G, Qin-yan Y. Natural organic matter (NOM) removal from surface water by coagulation. J Environ Sci. 2005;17(1): 124–7.
11. Mcdonald S, Pringle JM, Bishop AG, et al. Isolation and seasonal effects on characteristics of fulvic acid isolated from an Australian floodplain river and billabong. J Chromatoqr A. 2007; 1153: 203–13.
12. Gao BY, Yue QY. Natural Organic Matter (NOM) removal form surface water by coagulation. J Environ Sci. 2005; 17(1): 124-7.
13. Aboul MYZ, Wells MJM. Assessing the trihalomethane formation potential of aquatic fulvic and humic acids fractionated using thin-layer chromatography. J Chromatoqr A. 2006; 1116: 272–6.
14. Hashemi H, Hajizadeh Y, Amin MM, et al. Macropollutants removal from compost leachate using membrane separation process. Desalination Water Treat. 2015; 57(16): 49-54.
15. Amin MM, Hashemi H, Bina B, et al. Pilot scale studies of combined clarification, filtration, and ultraviolet radiation systems for disinfection of secondary municipal wastewater effluent. Desalination. 2010; 260 (1-3): 70-78.