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Characterization of humic acid extracted from aqueous solutions with polymer inclusion membranes

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ABSTRACT

Humic acid was extracted from the aqueous solution of sodium humate by using polymer inclusion membranes. Sodium humate was obtained by treating lignite from Kahramanmaraş Afşin-Elbistan Region in Turkey. Lignite can be evaluated as humic acid source for organic fertilizer. PIMs were prepared by using cellulose triacetate as polymer, a cationic carrier, tricaprilmethylammonium chloride (Aliquat-336), modifier tributyl phosphate and plasticizer 2-nitrophenyl pentyl ether. A permeation cell was used for the separation fulvic and humic acid from sodium humate. In our study, the separation of humic and fulvic acids from polymeric membranes was investigated and partial separation was observed. Although, HCl is used in the separation process in the classical methods, we did not follow the same procedure in our method. The advantage of the new method is that it is a one-step separation and a clean process. Surface morphology of membrane and properties of extracted humic samples were compared with Fluorescence, UV, SEM and FTIR analysis.

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1. Introduction

Humic substances are heterogeneous mixture of both aliphatic and aromatic high molecular weight organic compounds, which are rich in content of oxygen containing functional groups [1]. Wide variety in the structural compounds of humic substances is the result of the random polymerization of variety of the decomposed material. In addition, the structure of the humic substances varies according to the outsourced method and source. This structural heterogeneity extremely obstructs structural and conformational characterization of humic materials. These contain almost 40–60% of the organic carbons dissolved in natural waters and 60–70% of the total organic carbon in the soils [2]. In humic substances, humic acid, fulvic acid and humin are the major fractions. Humic acids redefined as yellow-brown to black brown substances of unknown constitution. Humic substances can be identified as functional according to their solubility in the water. Humic acid is also an important class of organic anion in natural waters [3]. Humic substances are operationally classified according to pH-dependent aqueous solubility. Humic acids do not dissolve in pH < 2 water solutions but they can dissolve in higher pH

values; fulvic acids can dissolve under any pH condition and humins do not dissolve at any pH value.

Humic acids have been extracted not only from soil but also from peat, brown coal, oxidized bituminous coal, and even from artificial materials obtained in the laboratory [4,5]. Humic acids can split off hydrogen ions and form typical salts with strong bases and usually is insoluble in water, soluble in alkali, and reprecipitated by acids. The alkali solubility of humic acid is due to carboxyl and phenolic hydroxyl groups, which account for about 22% of the weight of the molecule. Humic substances are usually negatively charged in aqueous solutions at neutral to high pH [6]. Applications of humic substances are available in agriculture, environmental and industrial areas.

In the environmental applications, the main role of the humic substances is taking toxic metals, anthropogenic organic chemicals and other contaminations from the water. It is seen that ion modifiers based on the calcium humate is suitable for the removal of iron, nickel, mercury, cadmium and copper from water. Humus based filters are developed sewage treatment with several applications [7].

Humic substances occur as natural water contaminants as the result of decomposition of plants. Although humic acid is not directly toxic, it can produce taste and smell [8]. Humic acid also produce disinfection side product, which can cause cancer via reaction with chlorine during the disinfection of drinking water. Natural waters can possess humic acid concentration below 10–15 mg/L.

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Adsorption, membrane separation, coagulation and more methods were used for the removal of the humic acid from waters [9]. Yu et al. [3] revealed that the Aliquat-336/ Na_2SO_4 a cloud-point extraction system is very efficient in extracting humic acid from aqueous media indeed. Among these processes, membrane technology has stood out with its low cost, and low energy consumption, also simplicity in processing and being environmentally compatible.

According to results of some studies, humic acid adsorption occurs both inside the pore and on the membrane surface [10]. Humic acid is mostly negatively charged in the solution due to carboxylic acid ($-\text{COOH}$) and phenol ($-\text{OH}$) functional groups [7]. Thus, in order to facilitate the adsorption of humic acid on the adsorbent surface via electrostatic force, typically surfaces with positively charged functional groups attract more interest [8]. However, in our study, lignites with low calorific value and used for heating and electricity production purposes from Afsin-Elbistan, regions of Turkey can be evaluated as humic acid source for organic fertilizer production and this means more added value into Turkish economy.

Humic and fulvic acid was transport in the stripping phase by carrier. Both surfaces of membranes and properties of extracted products were characterized using Fluorescence, UV, SEM and FTIR techniques.

Humic acid can be thought of as grouped molecules in certain molecular weight regions. This differentiation is entirely due to the process of humic acid formation. Because of the strong interactions between the polar groups of fulvic and humic acid molecules, it is difficult to separate from each other. There has been no report in the literature that pure humic and fulvic acid are completely separated from each other. We observed the separation of humic and fulvic acids by polymeric membranes, depending on the time.

2. Experimental

2.1. Chemicals and materials

The chemicals; cellulose triacetate (CTA), 2-nitrophenyl pentyl ether (2-NPPE) in the experiments were provided from Fluka, tributyl phosphate (TBP), dichloromethane, NaOH were provided from Merck, extractant (Aliquat 336) Cognis Corp. (Germany). Commercial humic acid was provided Sigma-Aldrich. Sodium humate is obtained by treating lignite from Kahramanmaraş Afsin-Elbistan Region with NaOH. All solutions were prepared in the deionized water.

2.2. Instrumental

The instruments used during analyzes were Perkin Elmer Spectrum Two for FTIR analysis, JEOL brand for SEM images.

Surface morphology of humic acids was researched by Scanning electronic microscope. The samples were previously covered with a thin Au layer. The structural information was investigated by Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR).

2.3. Membrane preparation

Membrane was prepared with casting method. It is dissolved in CTA (480 mg) 70 mL dichloromethane. 0.1–0.5 mL 2-NPPE was added at the next phase. Aliquat 336 and TBP were added to solution after they were mixed. This mixture was poured to square container (24 cm \times 24 cm) slowly. Solution that poured to the glass was remained at the ambient temperature for a night for evaporation of organic solvent. After evaporation of solvent, it was washed with distilled water. Then membrane was removed from the container [10].

2.4. Transport experiment

A Pyrex glass cell with two-compartment which connected with a flat sheet membrane with the area of 12.56 cm^2 was used to study of the transportation process of humic acid ions from aqueous solutions via polymer inclusion membrane. The membrane used for this purpose is a polymeric film. The same amount of the feed and strip phase (250 mL each) were used in permeation cell [11]. To make the aqueous solution sodium humate is dissolved in distilled water and 0.25 M NaOH solution was used to make the stripping solution.

3. Results and discussion

The performance of a membrane can be affected by the chemical solution characterization. For example, the membrane can perform differently due to charge change caused by the chemical solution. Elimelech and Childress [12] showed that in the pH range from 3 to 11 cellulose acetate membranes have negative surface charge and with increasing the pH membrane charge becomes more negative. Furthermore, negative solution ionic strength causes membrane to show negative surface charge that is due to the adsorption of anion from the solution to the membrane surface [13].

The streaming potential experiments demonstrated that humic macromolecules were adsorbed onto the surface of cellulose acetate membranes and changed their surface charge noticeably [12]. The solution pH changes the structure of the humic and fulvic acid molecules. All the carboxyl groups are in protonated form and increase in pH value of solution causes deprotonation of those groups [14]. At low pH and high concentration values, humic and fulvic acid molecules show a compact structural form, but at high pH and low concentrations, their structure becomes linear [15].

Aliquat 336 is very efficient in extracting humic acid from aqueous media. Humic acid forms an ion- pairing with cationic carrier and binding. The same situation was also observed by Yu et al. [3].

3.1. Fluorescence and UV analysis

Fluorescence spectra of molecular size fractions of extracted humic acid samples were shown in Fig. 1. Intensities of peaks increase with elapsed extraction time. Humic acid samples have first peak around 400 nm. Second sample has two peaks. Fulvic acid (FA) content influenced emission peak at 360 nm and shoulder at 420 nm and indicated simply phenolic compounds. In generally the high FA content corresponded with higher relative fluorescence intensity at 360 nm (Fig. 1) [16,17].

Fig. 1 shows only the peaks belongs to the sample. The humic and fulvic acid samples absorb in a broad range and for fluorescence studies 315 nm was selected for the excitation of samples. The fluorescence peaks were appeared around 350 nm for those samples. In the comparison of acquired spectra at different collection times, fluorescence spectra shows intensity increase and red shift and this is most probably due to the increasing humic acid amount in the medium. Fig. 2 also shows the UV analysis of same concentration changes in stripping region. The spectra were collected after 2, 4, 10, 24, 46 and 70 h later. The spectra show slow absorption increase around 270 nm which is most probably due to the aromatic structures in the solution medium. At the beginning of stripping, only small molecules which are fulvic acid molecules pass from membrane and this continues till the 10th hour of process. After the 10th hour concentration of aromatic groups increases because of humic acid molecules. The main problem for the separation of humic and fulvic acids is that the bigger molecules also can pass from the membrane during the

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