



# Adsorption of nitroaniline positional isomers on humic acid-incorporated monolithic cryogel discs: Application of ligand-exchange concept



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## ARTICLE INFO

**Keywords:**  
Adsorption  
Cryogel  
Humic acid  
Ligand-exchange  
Monolithic adsorbent  
Nitroaniline

## ABSTRACT

Adsorptive removal of some nitroaniline positional isomers was studied by using a humic acid-cryogel based monolithic adsorbent (MLHA). Monolithic material was characterized by FTIR and SEM techniques. The adsorbent was turned into a ligand exchanger form (i.e. Cu-MLHA) by Cu(II) loading. The amount of Cu(II) bound to the monolithic discs was determined by AAS analyses. The effect of contact time and initial nitroaniline concentration on adsorption was studied, and the fit of some isotherm models was analyzed. Maximum observable adsorption capacities recorded on Cu-MLHA were found to be around 150–180 mg/g, and the capacities decreased in the order 3-nitroaniline > 4-nitroaniline > 2-nitroaniline.

## 1. Introduction

Nitroanilines (NA) are one of the most widely used classes of aromatic amines in the industry for the production of dyes, plastics, pharmaceuticals, antioxidants and agrochemicals. Due to their extensive use in the industry (and their high solubility in water), the leakage of nitroanilines into water resources inevitably occurs, and this causes serious ecological and health problems [1–6]. Moreover, these highly toxic chemicals threaten the health of living-beings for a long time period because of their high stability in the environment [3,5,7]. For this reason, the removal of nitroanilines from water resources and wastewaters is deemed important.

Biodegradation [5,8], photocatalytic degradation [4], and adsorption are some popular methods being used to overcome undesired effects of nitroanilines. Among the applied methods, adsorption offers inexpensive and much more effective manners [3]. The efficiency of an adsorption process is mostly determined by the adsorbent used, and thus adsorbent is accepted as the key factor in adsorption process. In the literature, there exist studies dealing with the potential use of various adsorbents for adsorptive removal of nitroanilines. Among the studied adsorbents activated carbon [9,10], gold nanoparticles [11,12], polymeric adsorbents [13,14], activated carbon fibers [15], and coal [16] can be mentioned.

Humic acid (HA) is a naturally-occurring biomacromolecule which has a complex macromolecular structure comprised of hydrophilic groups (e.g. carboxyl, carbonyl, phenolic hydroxyl, alcoholic hydroxyls, amine, amide, and etc.) covalently bonded to a hydrophobic network made up of aromatic, aliphatic, and heterocyclic units [17–19]. Hence,

HA exhibits a multifunctional character that enables HA to interact with different kind of chemical species [20,21]. Interaction capability of HA is mostly ascribed to acidic functional groups (i.e. –COOH and phenolic –OH) which can bind metal ions through ion-exchange and complex formation mechanisms [17]. Owing to this property, HA-derived adsorbents have been extensively studied in adsorption of metal ions [22–25].

Owing to tight metal-binding character of HA, HA-derived adsorbents were thought to have a potential in ligand-exchange process, too. And, it is seen in the literature that after loading a metal ion, HA-immobilized silica has been efficiently used as a stationary phase in ligand-exchange chromatography of nucleosides and nucleobases [20]. This approach, which is based on ligand-exchange concept, may be useful in adsorptive removal of nitroanilines, too.

The researchers dealing with HA-derived adsorbents usually point out a problem arising from the solubility of HA in water and thus emphasize a very limited application range for direct use of solid HA as an adsorbent. To overcome/minimize the solubility risk of HA in water, and to turn it into a less soluble form, some processes (e.g. insolubilization, immobilization) have been proposed in the literature [25,26]. It has been reported that immobilization has some advantages over insolubilization to prepare a HA-derived adsorbent with a controllable particle size and shape [20,26]. It is seen in the literature that immobilization of HA to different support materials, such as silica [26–29], polymers [30], and hematite particles [31], has been successfully performed. However, the obtained HA-derived adsorbents are seen to be mainly in granular forms and the applicability of a monolithic support in HA immobilization has not yet been fully studied. On

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the other hand, in application, HA-incorporated monolithic adsorbents might offer much more advantages (such as preparation in a desired shape, ease of separation of adsorbent from the suspension, better adaptability to column processes, and etc.) over those in granular forms.

A class of hydrogels prepared at subzero temperatures are called “cryogels” and these polymeric materials have been extensively used (as support materials) in separation and purification processes like adsorption and chromatography [32–45]. Their supermacroporous morphology facilitates the transport of (even) high-molecular weight species (e.g. proteins) through the pores, efficiently. Moreover, cryogels can easily be prepared through inexpensive manners with little use of chemicals. Owing to their morphology and the suitability of their chemistry to further surface modifications, cryogels are thought to be nice platforms for the immobilization of macromolecules like HA. In the literature, there are few studies [46] dealing with the preparation of HA-immobilized cryogels, whereas such a material might have a great application potential in separation and purification of chemicals and biologically-important species. In one of the recently published studies [46], HA was bonded to a cryogel matrix in presence of Cu(II) ions, and protein interaction with the obtained monolith was studied. However, the hydrolytic stability of the prepared material is seen to be poor, so that HA leakage from the adsorbent has been evidenced [46]. Recently, a highly stable HA-incorporated monolithic material (i.e. HA-incorporated poly(2-hydroxyethyl methacrylate, MLHA) has been developed first by our group (A.E. Özkan, I. Guven, O. Gezici, *Protein ion-exchange chromatography on a biomacromolecule-immobilized monolithic cryogel, 2016, Unpublished*). The prepared monolith has been applied in protein ion-exchange chromatography as a stationary phase, successfully. Despite the material reported in [46], MLHA exhibited an extreme hydrolytic stability even at pH 11. Hence, good mechanic and hydrolytic stability, multifunctionality, and preparation through inexpensive manners by using a naturally-occurring biomacromolecule, i.e. HA, are some aspects making MLHA a nice monolithic material. For this reason, such a material donated with different kind of functionalities is believed to have a high potential when used as a solid phase in separation and purification processes of different types of chemical species. Due to its interaction capability with chemical species through various interaction mechanisms (e.g. ion-exchange, ligand-exchange, hydrogen bonding, hydrophobic interactions,  $\pi$ - $\pi$  interactions, etc.), MLHA deserves much more attention to study its usability as a monolithic separation medium.

In the present study, MLHA was turned into a ligand exchanger form by loading of Cu(II) and used as a new separation medium for the adsorptive removal of some NA positional isomers. Electron-donor groups in nitroanilines led us designing the study on the basis of ligand-exchange concept, and for this reason Cu(II)-loaded form of the monolithic adsorbent has been employed throughout the study. To the best of our knowledge, this is the first study dealing with the application of ligand-exchange concept on a HA-incorporated monolithic cryogel. The study is believed to have a pioneering role in design and preparation of new-type HA-derived adsorbents.

## 2. Experimental

### 2.1. Chemicals

The chemicals used throughout the study and the purpose of their use are tabulated in Table 1. All the chemicals and reagents are of analytical reagent grade purity and used as received. Aldrich HA was used after a purification process which was basically applied to remove alkali-insoluble particles according to a known procedure [19].

### 2.2. Instruments and apparatus

FTIR spectroscopy analyses were performed by an ATR-FTIR instrument (Perkin-Elmer 400 model), and the spectra were taken with

4 cm<sup>-1</sup> resolution. Scanning Electron Microscopy (SEM) images were recorded on a Zeiss Evo Basic model instrument. The images were taken under vacuum ( $1.32 \times 10^{-2}$  Pa) after preparation of the samples by platinum sputtering. pH measurements were done by using a combination pH measurement system (Mettler-Toledo). Cryogellation process was performed at -20 °C in a deep freezer (Uğur). A UV-vis spectrophotometer (PG Instruments T80 model) was utilized in the stability tests of HA-incorporated monoliths. Amount of Cu(II) bonded to MLHA was determined by an Atomic Absorption Spectroscopy (AAS; Shimadzu) instrument. The concentration of nitroanilines after adsorption process was determined by an HPLC system (Agilent 1260) with UV detection at 254 nm. A C-18 column (4.6 × 150 mm) was used in the chromatographic analyses. Freshly prepared ultrapure water (18.3 MΩ.cm) was used throughout the study.

### 2.3. Preparation and characterization of monolithic discs

A facile procedure (A.E. Özkan, I. Guven, O. Gezici, *Protein ion-exchange chromatography on a biomacromolecule-immobilized monolithic cryogel, 2016, Unpublished*), which has been recently developed by our group, has been followed to prepare HA-incorporated monolithic adsorbent (MLHA). Briefly, 0.6 mL HEMA and 0.10 g MBAAm were dissolved in degassed water and the obtained solutions were mixed (in an ice-bath) to obtain a 10 mL mixture. To this mixture, 0.02 g APS was added and the mixture was stirred for further 5 min in an ice-bath. Finally, 40 µL TEMED was poured into this mixture to initiate the radicalic polymerization, and required amount of solid HA (0.01 g HA/1.0 mL final mixture) was immediately added to the final mixture. The obtained monomer solution was quickly poured into empty columns with 5.0 mm i.d. Afterwards, the columns were put into a freezer and kept at -20 °C for 24 h. The prepared monoliths were put out of the freezer for thawing at room temperature. After thawing, the monoliths were consecutively rinsed with 10% (v/v) ethyl alcohol solution, water,  $1.0 \times 10^{-3}$  M NaOH (in 1.0 M NaCl), and plenty of water. Prepared monolith was cut into 2 mg discs having dimensions of  $5.0 \times 2.0$  mm (diameter × thickness). To 50 mL 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub> solution, 20 pieces of MLHA discs were added and agitated on an orbital shaker at room temperature for 24 h. Afterwards, the discs were thoroughly washed with water to remove unbounded Cu(II) ions. Prepared discs, Cu-MLHA, were used in adsorption experiments.

Immobilization of HA to the monolithic support, ML, was evaluated by FTIR spectroscopy and SEM. FTIR spectra were compared with each other to evaluate the success of HA immobilization. Changes in microstructure of the monolith before and after HA immobilization were evaluated by analyzing the SEM images. The stability tests were also performed to evaluate the hydrolytic stability of MLHA, and thus to see possible risks of adsorbent dissolution (i.e. HA leakage) under the studied experimental conditions. For this purpose, known amount of MLHA was put into an aqueous solution of pH 11 for 72 h, and afterwards the effluent was analyzed by UV-vis spectroscopy at 410 nm.

### 2.4. Adsorption of nitroanilines

The adsorption of NA on Cu-MLHA was conceptualized on the basis of ligand-exchange mechanism as illustrated in Fig. 1. Batch adsorption experiments were done to investigate NA adsorption to Cu-MLHA. For this purpose, to a 15 mL of NA solution, one piece of Cu-MLHA disc was added and the mixture was agitated on an orbital shaker (Heidolph). After a predetermined time, the disc was put out of the NA solution, and the remaining solution was analyzed by HPLC to find changes in NA concentration. Amount of NA adsorbed by Cu-MLHA was calculated from the difference according to the following relation:

$$q = \frac{(C_0 - C_f) \times V}{W} \quad (1)$$

where  $q$ ,  $C_0$ ,  $C_f$ ,  $V$ , and  $W$  denote amount of NA adsorbed per g of

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