Adsorption of Humic Acid from Water Using Chemically Modified Bituminous Coal-based Activated Carbons

Habuda-Stanić, Mirna; Tutić, Ana; Kučić Grgić, Dajana; Zeko-Pivač, Anđela; Burilo, Anamarija; Paixão, Susana; Teixeira, Veronica; Pagaimo, Mariana; Pala, Aysegul; Ergović Ravančić, Maja; ...

Source / Izvornik: **Chemical & biochemical engineering quarterly, 2021, 35, 189 - 203**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

https://doi.org/10.15255/CABEQ.2021.1933

Adsorption of Humic Acid from Water Using Chemically Modified Bituminous Coal-based Activated Carbons

M. Habuda-Stanić,[a,*] A. Tutić,[b] D. Kučić Grgić,[c] A. Zeko-Pivač,[a]
A. Burilo,[a] S. Paixão,[d] V. Teixeira,[d] M. Pagaimo,[d]
A. Pala,[e] M. Ergović Ravančić,[f] and M. Šiljeg[g]
[a]Josip Juraj Strossmayer University in Osijek, Faculty of Food Technology
Osijek, Franje Kuhača 18, 31000 Osijek, Croatia
[b]Bor-plastika d.o.o. Glavna 2, 31309 Kneževi Vinogradi, Croatia
[c]University of Zagreb, Faculty of Chemical Engineering
and Technology, Marulićev trg 19, 10000 Zagreb, Croatia
[d]Escola Superior de Tecnologia da Saúde de Coimbra,
Rua 5 de Outubro, 3046-854 Coimbra, Portugal
[e] Dokuz Eylul University, Department of Environmental
Engineering, 35160 Buca, Izmir, Turkey
[f]Polytechnic in Požega, Vukovarska 17, 34000 Požega, Croatia
[g]University North, Jurja Križanića 31b, 42000 Varaždin, Croatia

doi: https://doi.org/10.15255/CABEQ.2021.1933

Original scientific paper
Received: February 18, 2021
Accepted: July 12, 2021

Humic acid (HA) impairs water quality due to its reactivity with many substances present in water. During the drinking-water treatment process and water distribution via water supply system, HA present in water may react with chlorine and other disinfects producing harmful disinfection by-products (DBPs), which are categorized by the International Agency for Research on Cancer (IARC) in groups 2A (probably carcinogenic to humans) or 2B (possibly carcinogenic to humans). Several studies have investigated and reported increased HA removal by iron-coated sorbents. Therefore, the aim of this study was to examine the removal of HA from water by two commercially available bituminous coal-based activated carbons (ACs), Cullar D (Cm) and Hydraffin 30N (Hm). Prior to testing the chosen adsorbents were chemically modified according to two protocols: (1) oxidation by acid mixture (m1), and (2) oxidation with acid mixture followed by iron-ions impregnation (m2). The batch adsorption tests were used to test their efficiency in HA removal under various values of process parameters (initial HA concentration, pH, contact time, adsorbent mass, and temperature). The results showed that up to 96 % of HA removal can be obtained by Cullar D modification Cm1, while maximum uptake of HA by Hydraffin 30N modification was achieved with Hm1 (62.1 %). After surface saturation with Fe^{3+} –ions (m2), both activated carbons showed similar and lower performances in HA removal (Cm2 up to 66.5 %, and Hm2 up to 50.3 %). FTIR analysis confirmed differences in modified AC structures, as well as favorable structure of Cm1 for HA adsorption.

Keywords:
drinking water, humic acid, adsorption, bituminous coal-based activated carbon, chemical modification

Introduction

Natural organic matter (NOM) is a complex mixture mostly consisting of the following humic substances: humin, humic acid (HA), and fulvic acid. Humic acid is one of the main constituents of NOM, and together with fulvic acid presents up to 80 % of the dissolved organics in natural waters. HA is not particularly toxic, but impairs the organoleptic properties of water. However, present in treated drinking water, HA reacts with chlorine and chlorine-based disinfects producing several different compounds, such as trihalomethanes (THMs), haloacetic acids (HAAs) and haloketones, classified as disinfection by-products (DBPs), which the International Agency for Research on Cancer (IARC) has categorized as probably carcinogenic to humans (group 2A) or possibly carcinogenic to humans (group 2B). Moreover, HA can also bind molecules

---

[*]Corresponding author: E-mail: mirna.habuda-stanic@ptfos.hr
Tel.: +385 31 224 326; Fax: +385 31 207 115

of pesticides and heavy metals on its surface, and, therefore, natural organic matter, and HA as part of them, should be removed during drinking-water treatment.[1]

Several technologies are known for removing HA from aqueous solutions, such as coagulation with flocculation, membrane filtration, ion exchange, and adsorption.[2]

Effective removal of NOM and HA is still a challenge for water treatment technologies. Conventional method of coagulation and flocculation is mostly used in many water treatment plants, but high efficiency was obtained when filtration by single-media and dual-media filters were used, as well as ion exchange, membrane filtration, advanced oxidation processes, and adsorption on granular activated carbon.[2–6]

Ion exchange presents an economically acceptable substitution for conventional HA removal, but is more suitable for smaller water-supply systems and a relatively lower initial HA concentration.[2] During the recent decade, membrane filtration has been tested in many studies for HA removal.[7] Its high efficiency, process simplicity, and the quality of the treated water caused a global trend of coagulation and flocculation replacement by membrane filtration. However, the main problem associated with water membrane filtration is the membrane fouling by NOM fractions. Therefore, as an optimal solution, many water treatment plants kept the coagulation and flocculation process as a raw water pretreatment step. In these cases, the efficiency of HA removal is mostly caused by the type of coagulant, process conditions, membrane type, and the characteristics of raw water.[2,7–9]

Due to low negative environmental footprint, HA removal by various types of advanced oxidation processes (AOPs) also came into the focus of many studies. AOPs are characterized by ability to form strong oxidizing hydroxyl radicals in water that oxidize and eliminate many different contaminants from raw natural water and wastewater.[2]

Recently, Salvestrini *et al.*[10] and Du *et al.*[11] reported efficient humic acid removal by electrochemical oxidation (EO). Salvestrini *et al.*[10] tested HA removal using platinum-coated titanium electrodes and reported rapid oxidation of HA into smaller molecules with lower aromaticity and conjugation degree, while Du *et al.*[11], testing the treatment of nanofiltration concentrate EO with a boron-doped diamond anode, obtained total decomposition of humic acids, antibiotics, and bacteria present in treated concentrate produced by membrane filtration.

Among them, adsorption is a commonly used and widely researched technology, since it is cost-effective, flexible, and easy to operate. Many researchers have tested various adsorbents and reported that materials such as activated carbons, clays, zeolites, and iron oxides can be applied for effective water treatment. Activated carbons are the most commonly used adsorbents due to their pore size distribution and large surface areas where the active sites of HA functional groups can attach.[12–15] Efficient adsorption of numerous compounds onto adsorbent is caused by a large number of functional groups on their surfaces, including the carboxyl, carbonyl, hydroxyl, lactone, and basic groups such as pyrrole, pyridine and amide groups.[15]

HA contains carboxylate groups as well as aliphatic and aromatic hydroxyl groups, negatively charged over the most of the pH range. Interaction between functional groups on the HA and charged surface sites on adsorbent is of particular importance for adsorption. Many research studies have reported that adsorption efficiency varies with the following key parameters: solution pH, adsorbent-adsorbate combination, adsorbent and adsorbate initial concentration, time of adsorbent and adsorbate contact, as well as temperature of water.[13,15,16]

Researchers have also reported that reaction active sites of the adsorbent surface and the functional groups of adsorbates can occur through electrostatic interactions, ligand exchange, cation bridging, H-bonding, hydrophobic interactions or Van der Waals attraction.[13–15]

Su *et al.*[17] tested and reported the results of their study conducted with aim to investigate the possibility of Cr^{3+}, Pb^{2+} and Cu^{2+} removal from wastewater by adsorption onto an insoluble humic acid/starch composite microspheres (HS-CM). They founded that HS-CM had adsorption capacity for all three tested metal ions above one-hundred mg g^{-1} even after five cycles of regeneration. Humic substances are recognized as the primary precursors of disinfectant by-products. HA reacts with halogens, mainly chlorine ion, during disinfection, forming THMs. $CHCl_3$ and $CHClBr_2$ are considered carcinogenic, while $CHBrCl_2$ is a mutagen that affects DNA. Therefore, HA concentration in water, as well as the presence of other NOM compounds in water increase the potential of DBPs formation.[17–19]

Many researchers have investigated the effects iron coating of various porous materials on their adsorption capacities during removal of pollutants from water, since studies have shown that iron oxide coating overwhelmed the surface electrical properties of the treated base material causing an increase in adsorption capacities of treated material.[19,20]

Kitis *et al.*[19] used natural pumice particles as base material for chemical modification and iron oxide coating. After modification, obtained iron-coated adsorbent was tested for NOM removal. The authors reported that iron-coated pumice particles showed significantly higher efficiency of NOM removal from water.

Ding *et al.*[20] prepared iron oxide-coated sand and tested NOM removal efficiency, and, although modification of base material caused no changes in the physical properties of adsorbent, faster initial NOM adsorption and increase in adsorption capacity of iron-coated adsorbent was reported.

Therefore, the aim of this study was to examine the removal of HA from water by two commercially available bituminous coal-based activated carbons (ACs), Cullar D (Cm) and Hydraffin 30N (Hm). In this study, two commercially available bituminous coal-based activated carbons, Cullar D (C) and Hydraffin 30N (H), were chemically modified using two protocols: (1) oxidation by mixture of HNO_3 and H_2SO_4 to obtain modification 1 (m1), and (2) oxidation by mixture of HNO_3 and H_2SO_4 followed by Fe^{3+} impregnation to obtained (m2). Both modifications were tested for humic acid removal efficiency and reduction in formation of disinfection by-products using absorbance ratio A_{254}/A_{203}, since this parameter is commonly reported as a good predictor of the trihalomethane formation potential (THMFP) during obligatory disinfection of drinking water.[21–24] Using batch adsorption tests, the efficiency of Cm1, Cm2, Hm1, and Hm2 in HA removal under various conditions (initial HA concentration, pH, contact time, adsorbent mass, and temperature) were tested. Fourier-transformed infra-red spectroscopy (FTIR) analysis was conducted in order to define a portion of surface changes, as well as the presence of surface functional groups in tested modified activated carbons.

Materials and methods

Chemical modification of activated carbons

Two commercially available granular bitumen-based activated carbons were used in this study: Hydraffin 30 N (Donau Carbon Corporation, Springfield, USA) and Cullar D (Culligan Italiana S.P.A., Cadriano, Italy). The characteristics of activated carbons used are presented in Table 1.

Prior to this study, Cullar D and Hydraffin 30N were tested in their non-modified forms at 25 °C, and results showed the following performances in humic acid removal: in test with various initial HA concentrations, Cullar D removed up to 11.3 %, and Hydraffin 30N removed up to 45.9 % of HA. Testing the effect of contact time at longest contact time (120 minutes) Cullar D removed 23.3 % and Hydraffin 30N 35 % of HA. Adsorption test conducted under various pH showed that maximum HA uptake occurred with Cullar D up to 66 % at pH 7.5. Hydraffin 30N also showed the maximum HA uptake of 56.4 % at pH 7.5. Experiments with various adsorbent doses showed that Cullar D could remove up to 63.4 % of HA at 10 g L^{-1}, while Hydraffin 30N removed 22.1 % of HA under the same experimental conditions. Details of the aforementioned tests are not presented in this paper.

Table 1 – *Characteristics of tested bituminous coal-based activated carbons*

	Hydraffin 30N	Cullar D
Origin material	bituminous	bituminous
Particle size (mm)	0.6 – 2.36	0.42 – 0.84
Total surface area (B.E.T.) (m^2 g^{-1})	900	1050
Density (kg m^{-3})	440 – 500	200 – 220
Iodine number	900	750
Water content (%)	5	3
Ash content (%)	12	15

Therefore, in order to increase their adsorption capacities, Cullar D and Hydraffin 30N were chemically modified via two protocols:

Protocol 1: 20 g of activated carbon was continuously mixed with 1 L mixture of conc. HNO_3 and conc. H_2SO_4 mixture (1:1) during 1 hour at room temperature, then separated from the acid mixture by filtration, washed with deionized water, dried at 105 °C, and stored in a desiccator.

Protocol 2: 20 g of activated carbon was continuously mixed with 1 L mixture of conc. HNO_3 and conc. H_2SO_4 mixture (1:1) during 1 hour at room temperature. Oxidized activated carbons were separated from the acid mixture by filtration, and then saturated with Fe^{3+} ions using a 0.1 M solution of $FeCl_3$, previously stabilized with acetate buffer (pH 3.6). Mixture of iron solution and ACs were constantly stirred for 24 hours at room temperature. Activated carbon was filtered again, dried at 105 °C, and stored in a desiccator.

Characterization of activated carbons

Unmodified and modified forms of the bituminous coal-based activated carbons, Cullar D and Hydraffin 30N, were characterized using Fourier-transformed infra-red spectroscopy and FTIR spectrophotometer Perkin Elmer, Spectrum One. Measurement was conducted in the range of 4000 cm^{-1} and 650 cm^{-1}, and for the transmission method between 4000 cm^{-1} and 400 cm^{-1} with a spectral resolution of 4 cm^{-1}. To increase the signal-to-noise ratio, each sample was recorded four times.

Experimental procedure

Humic acid was purchased from Sigma Aldrich (Germany). Stock solution of HA was prepared by dissolving 1 g of solid HA in 1 L of deionized water at room temperature. The adsorption experiments, as a function of initial HA concentration, pH value, adsorption time, adsorbent mass, and temperature, were conducted using batch experiments. The stock solution was diluted with deionized water to give the desired concentrations of HA (1, 3, 5, 7, 9, 10 mg L^{-1}). The initial pHs of the solutions (4.5, 5.5, 6.5, 7.5, 8.5, 9.5) were adjusted by adding NaOH and/or HCl solutions at the beginning of the experiments. No further pH regulation or measuring during the adsorption processes was conducted in this study. The pH was checked and measured with a pH-meter.

Modified activated carbons (Cm1, Cm2, Hm1 and Hm2) were weighed on an analytical laboratory scale. Test suspensions were obtained by adding 0.05, 0.10, 0.15, 0.25, 0.50 or 1.00 g of activated carbon into 100 mL HA solution of a certain concentration. The adsorption involved shaking at 120 rpm in thermostatic water bath for a specific time (5, 15, 30, 60, 90, 120 min). All experiments were conducted at 25 °C and 35 °C. Samples were filtrated through 0.45 μm filter paper. The HA concentrations and THMFP reduction were determined by UV spectra using UV/Vis spectrophotometer Specord 200 Analytik Jena AG at wavelengths 254 nm and 203 nm in 1 cm quartz cell.

All experiments were performed in triplicate and average values were used for calculations.

Obtained data were processed and analyzed using the software system Statistica 13.3 (Statsoft Inc.) in order to calculate the mean values of UV$_{203}$ and UV$_{254}$, i.e., HA concentration before and after adsorption. Obtained mean values were further used for calculations.

The percentage of HA removal (%) was calculated from initial HA concentration (γ_0, mg L^{-1}), and final HA concentration (γ_e, mg L^{-1}) according to Eq. (1):[10]

$$R(\%) = \frac{(\gamma_0 - \gamma_e)}{\gamma_0} \cdot 100 \tag{1}$$

The adsorbed amount of HA per unit weight of the activated carbon sample, known as adsorption capacity, was calculated according to Eq. (2) as follows:

$$q_e = \frac{(\gamma_0 - \gamma_e) \cdot V}{m} \tag{2}$$

where q_e is adsorption capacity, mg g^{-1}; V is the volume of suspension, L, and m is the mass of tested activated carbons, g.[11]

All chemicals used in this study were of analytical grade.

Adsorption isotherms

The adsorption capacity is the value that gives information about the feasibility of the adsorbents for removing the pollutant from water. The Freundlich and Langmuir adsorption equations were employed to determine adsorption capacities of modified activated carbons at 25 °C.

Freundlich adsorption isotherm

Freundlich isotherm model describes an adsorption in multilayer form at a heterogeneous surface. The Freundlich isotherm is usually presented as:[26,27]

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

i.e., in linearized form:

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \tag{4}$$

where q_e is the amount of HA adsorbed per unit weight of the adsorbent at equilibrium (mg g^{-1}), and C_e is the equilibrium concentration of HA solution (mg L^{-1}). The Freundlich constants K_F and n (as $1/n$) are measures of adsorption capacity (mg g^{-1}) and adsorption intensity or surface heterogeneity.

Langmuir adsorption isotherm

Langmuir adsorption isotherm describes an adsorption in monolayer form, and is usually presented as:[26,28]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

i.e., in linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \tag{6}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of ion adsorbed (mg g^{-1}), q_m is q_e for a complete monolayer (mg g^{-1}), and K_L is adsorption equilibrium constant (L m g^{-1}). The constants q_m and K_L can be obtained from a linearized form of Eq. 6 by the slope of the linear plot of C_e/q_e versus C_e.

Results and discussion

Characterization of activated carbons

To obtain a clearer understanding of the activated carbons structure characteristics, and the effects of modifications and the mechanism of HA adsorption onto the modified activated carbons,

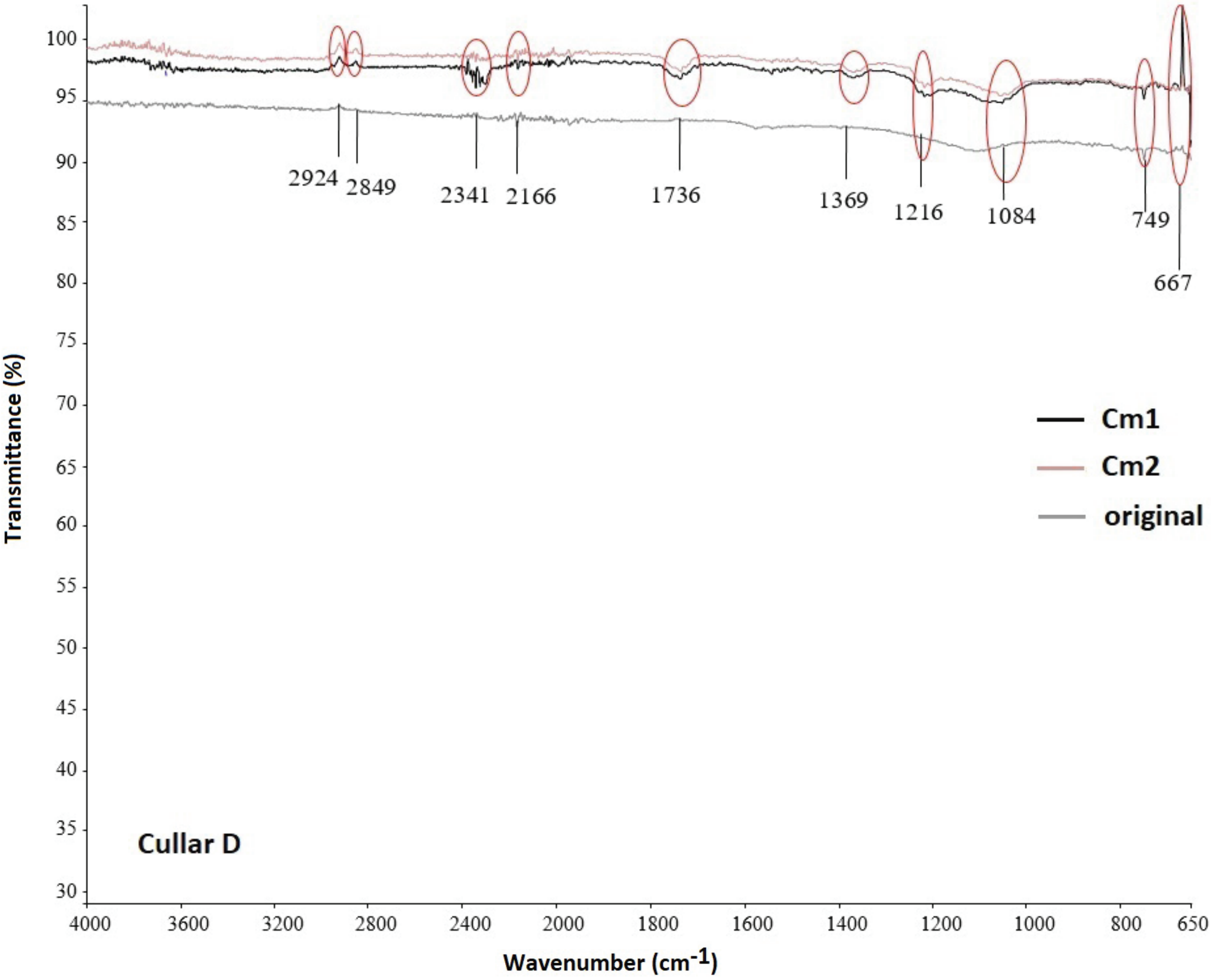

Fig. 1 – *FTIR spectrum of activated carbon Cullar D in original, Cm1 and Cm2 forms*

FTIR analysis was carried out. Obtained FTIR spectra are shown in Fig. 1 and Fig. 2.

Fig. 1 shows the FTIR spectrum of activated carbon Cullar D, before modification (original) and after modification with a mixture of acids (Cm1), and with a mixture of acids and $FeCl_3$ solution (Cm2). After the modification in both cases, there were new peaks and an increase in intensity. HNO_3 and H_2SO_4 as strong oxidants, increased the amount of oxygen in the functional groups of the sample. This was evident by the observed bands that had formed after acid treatment at 2800–3200 cm^{-1} belonging to O–H, and at 1650–1750 cm^{-1} belonging to C–O and C=O groups. A new band appeared at 2341 cm^{-1}, which was attributed to the aliphatic C–H stretching such as in an aromatic methoxyl group, methyl and methylene groups of side chain. The sharp bands occurring around 1100–1700 cm^{-1} were caused by C–O and COOH groups that were formed after oxidation.[29] Finally, low-intensity bands at 749 and 667 cm^{-1} were ascribed to the out-of-plane bending vibrations of aromatic C–H. Other studies reported bands at 557 and 465 cm^{-1} associated with the Fe–O vibrations bonds in Fe_3O_4.[3]

Fig. 2 shows the FTIR spectrum of activated carbon Hydraffin 30N, before modification and after modification with a mixture of acids (Hm1), and with a mixture of acids and $FeCl_3$ solution (Hm2). After modification, Hm1 and Hm2 had significantly different intensity of new peaks. The modification with a mixture of acids (Hm1) and with a mixture of acids and $FeCl_3$ solution (Hm2) caused appearance of new peaks and/or a stronger intensity of already existing ones. As in the case of Cm1 and Cm2, treatment of Hydraffin 30N increased the amount of oxygen existing in the functional groups of the sample, which can be concluded from the intensity of bands formed after first modification at 2800–3200 cm^{-1} belonging to O–H, and at 1650–1750 cm^{-1} belonging to C–O and C=O groups. A new band at 2341 cm^{-1} can also be observed in Fig. 2 (presence of aromatic methoxyl, methyl and methylene groups), but with lower intensity in compilation with Cullar D modification. The difference in

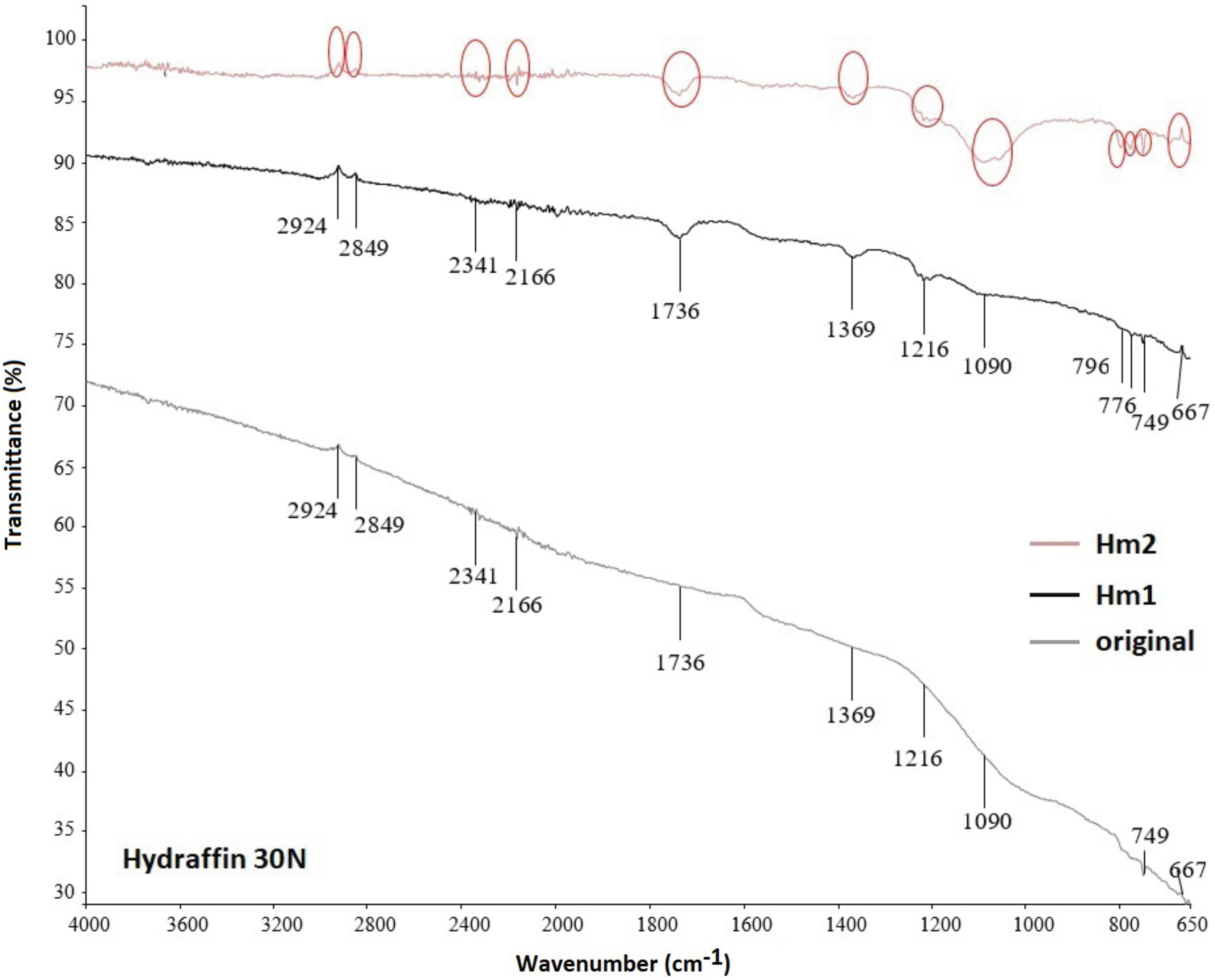

Fig. 2 – *FTIR spectrum of activated carbon Hydraffin 30N in original, Hm1 and Hm2 forms*

the intensity of Hm1 and Hm2 bands occurred after oxidation in the range of 1100–1700 cm^{-1} implying higher number of C–O and COOH groups in the structure of Hm2. The same changes are noted with the low-intensity bands (749 and 667 cm^{-1}), which can also be attributed to Fe–O vibration bonds in Fe_3O_4.[3]

Comparing all forms of Cullar D and Hydraffin 30N, it was observed that the transmission of peaks in samples Cm1 and Cm2 were higher than in samples Hm1 and Hm2. The transmission of peaks in samples Cm1 and Cm2 was almost equal. Analyzing the characteristics of Hydraffin 30N modifications, there was a large difference in peak intensity between Hm1 and Hm2.

Effect of adsorbent mass on HA removal

To optimize the mass of activated carbon for HA adsorption, the experiments were conducted with different masses of Cm and Hm ranging from 0.05, 0.10, 0.15, 0.25, 0.50 to 1.00 g, and the conditions already fixed for the adsorption process (initial HA concentration 5 mg L^{-1}, solution pH 7.5, temperature 25 °C and 35 °C, and adsorption time 120 min, 120 rpm). Obtained results are present in Fig. 3.

In theory, as the adsorbent's dosage increases, so does the surface area and the number of active sites, which results in the increasing of HA percentage removal.[21,24] As shown in Fig. 3, an increase in adsorbents dosages increased the rates of HA removal for all four tested adsorbents. The highest HA removals were obtained when dosage of 1 g/100 mL were used at 35 °C. Comparing the efficiencies of modifications, more efficient removal of HA were obtained with activated carbons modified according to Protocol 1. Adsorbent Cm1, at highest tested dose of 10 g L^{-1}, removed over 96 % of HA at 35 °C (Fig. 3a), while Hm1 (Fig. 3b) removed max 58.2 % of HA under the same experimental conditions. Amount of adsorbed HA per unit mass of adsorbent increased with dosages as the result of higher total number of active adsorption sites, but

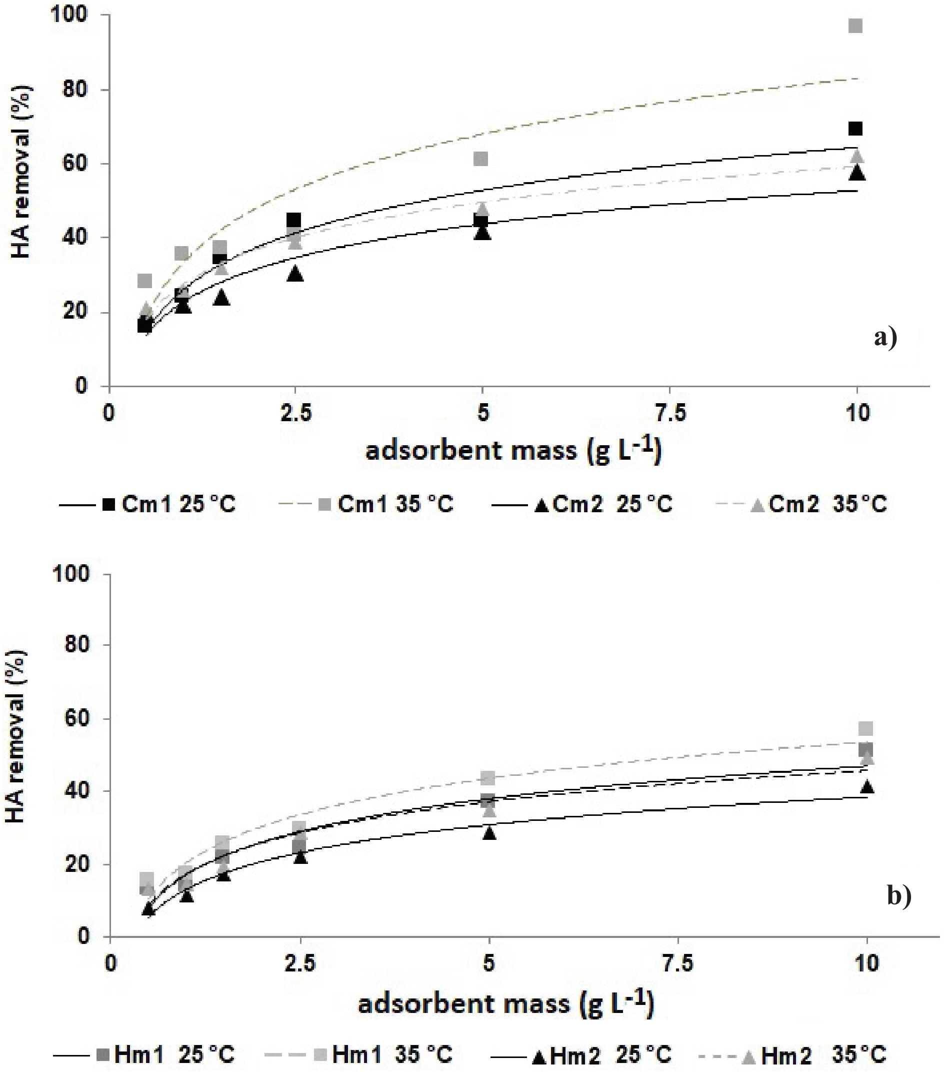

Fig. 3 – *Effects of adsorbent mass (a) Cm1 and Cm2, and (b) Hm1 and Hm2 on HA removal (γ_{HA}= 5 mg L^{-1}, T = 25 °C and 35 °C, $V_{solution}$ = 100 mL, t = 120 min, 120 rpm)*

significant improvement in the HA removal were observed only when the dosage of 10 g L^{-1} Cm1 was tested. For further tests, adsorbent dosage of 1 g L^{-1} was chosen.

Effect of initial HA concentration

The effects of the initial HA concentrations on humic acid adsorption onto tested modified activated carbons were evaluated at pH 7.5 and two different temperatures (25 °C and 35 °C). Tests were conducted using 0.1 g of activated carbon for 100 mL of solution with 1, 3, 5, 7, 9, and 10 mg L^{-1} initial HA concentrations. Samples were shaken at 120 rpm, for 120 min. Fig. 4 shows obtained results of HA removal by Hm1, Hm2, Cm1 and Cm2 at 25 °C and 35 °C.

Many adsorption studies have emphasized the relation among the driving force for the pollutant mass transfer between the aqueous and solid phase of the initial pollutant concentration.[30–32] As may be observed in Fig. 4a and 4b, adsorption capacities of all tested activated carbons increased with initial HA concentration. The maximum adsorption capacities were achieved with activated carbons modified via Protocol 1, and the positive effect of higher temperature on HA adsorption is also notable. The highest adsorption capacity of 0.18 mg g^{-1} showed Cm1 at 35 °C and 7 mg L^{-1} of HA, while among Hydraffin 30N modifications, the highest adsorption capacity was observed when Hm1 was tested at 35 °C and 10 mg L^{-1} of initial HA. Obtained results implied that the adsorptive removal of HA by Cm1, Cm2, Hm1 and Hm2 was concentration-dependent. Similar pollutant behavior during adsorption process was reported by Baek *et al.*[33] They attributed positive correlation between initial concentration and removal efficiency with the higher driving force provided to overcome all mass transfer resistances of the pollutant between the liquid and solid phase.

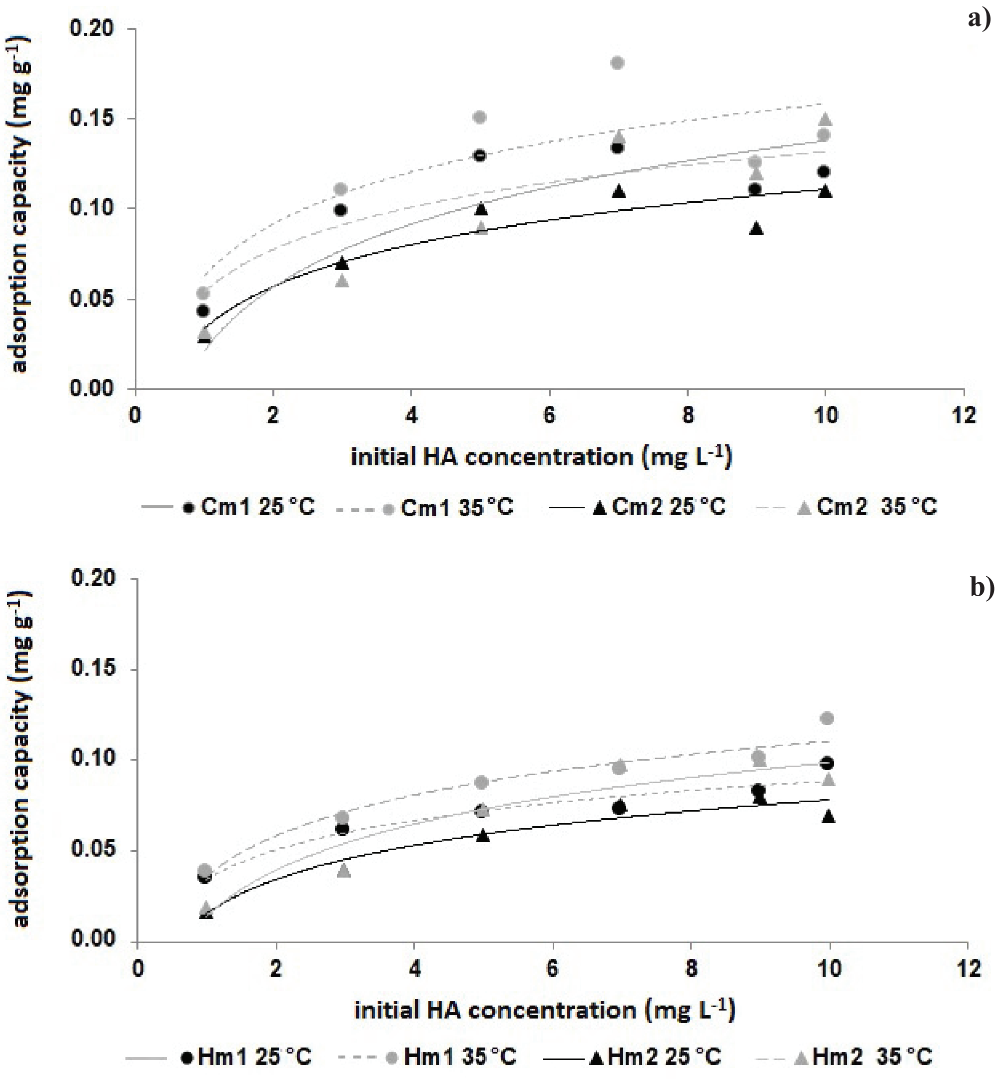

Fig. 4 – *Effects of initial HA concentration on adsorption capacity of (a) Cm1 and Cm2, and (b) Hm1 and Hm2 (γ_{ads}= 1 g L^{-1}, T = 25 °C and 35 °C, $V_{solution}$ = 100 mL, t = 120 min, 120 rpm)*

Effect of solution pH

The pH value has a strong impact on efficiency of most adsorption processes, since it determines the surface charge of molecules. Noorimotlagh *et al.*[21] reported that electrostatic, hydrophobic, and H-bonding interactions responsible for HA adsorption are strongly dependent on the solution pH. The effect of pH on the removal of HA from aqueous solution was studied at 25 °C and 35 °C.

Prior to the experiments, initial pH values were adjusted at 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5. The tests were performed with 1 g L^{-1} of modified activated carbon. Initial HA concentration was 5 mg L^{-1}. Samples were shaken at 120 rpm for 120 min, and obtained results are shown in Fig. 5.

Protonated adsorbent surface usually enhance many pollutant bindings, and, as the consequence of this phenomena, as Fig. 5 shows, for all tested modified activated carbons, maximum HA removal occurred at pH 4.5. Further increase in pH caused a decrease in HA uptake, while higher water temperature had a positive effect on HA removal. As Fig. 5a and 5b presents, the effect of pH change on HA adsorption rate was more significant in the pH range from 4.5 to 6.5, while changes in initial pH of the solutions in the range from 6.5 to 9.5 caused no stronger reduction in HA removal. The highest HA removals at all tested pH values and both temperature regimes, when compared to other modifications, were achieved with Cm1. The decrease in HA adsorption with increasing pH suggest that electrostatic interaction plays a role in adsorption process.[3] Namely, the low efficiency of HA removal at higher pH values can be explained with process of deprotonation of functional groups present in all modified activated carbon surfaces.[14,31,32] According to Noorimotlagh *et al.,*[21] the increase in the electrostatic repulsion force of HA decreases hydrophobic and hydrogen-bonding interactions, while Barhoumi *et*

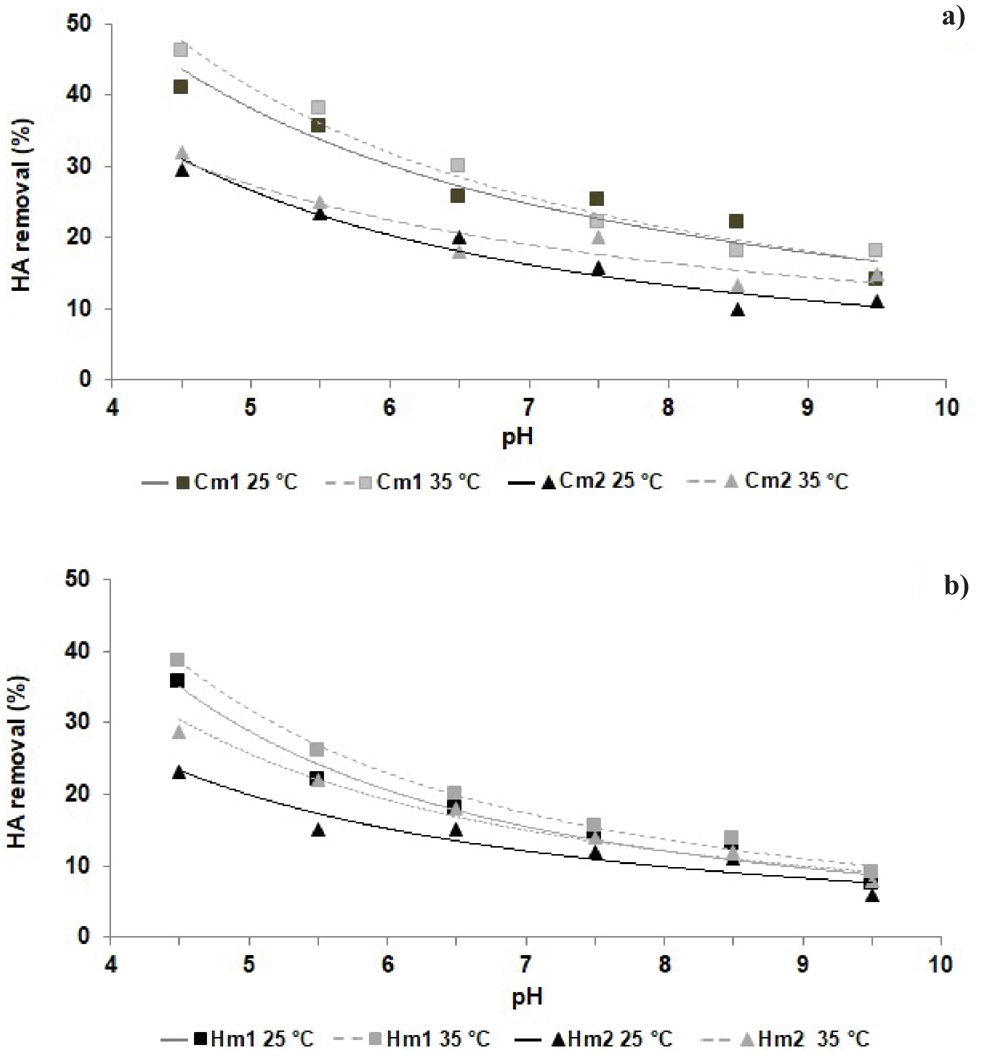

Fig. 5 – *Effects of pH on HA removal using (a) Cm1 and Cm2, and (b) Hm1 and Hm2 (γ_{HA}= 5 mg L^{-1}, γ_{ads}= 1 g L^{-1}, T = 25 °C and 35 °C, $V_{solution}$ = 100 mL, t = 120 min, 120 rpm)*

al.[18], emphasized that pH increase causes the surface to become more negatively charged and less attractive to the HA species.

Soleimani *et al.*[34] also tested HA removal by modified biosorbent, pumice stone. They reported the same relation between HA removal efficiency and pH value. The authors explained the positive effect of lower pH on HA removal efficiency by quicker diffusion of humic acid into adsorbent structure, and the changes in the diffusion properties of HA at lower pH values.

Effect of contact time

The effect of contact time on the HA removal from water using four types of modified activated carbons was determined within following contact time intervals: 5, 15, 30, 60, 90 and 120 minutes. Tests were performed at 25 °C and 35 °C at fixed adsorbent dosage of 0.1 g, pH 7.5, and initial HA concentration of 5 mg L^{-1}. Samples were shaken at 120 rpm for 120 min. The final HA concentrations as function of time are shown in Fig. 6.

As Fig. 6a and 6b shows, the increase in contact time increased HA removal by all tested adsorbents at both tested temperatures. However, two phases of adsorption dynamics, fast and slow, are noticeable in both Fig. 6a and 6b, as well as their lengths and similarities related to type of AU used as base material. Namely, the phase of fast adsorption occurred within the first minutes of contact between HA and Hm1 and Hm2, while in the case of HA removal by Cm1 and Cm2, equilibrium was reached almost after 100 minutes.

A stronger effect of contact time on HA uptake was observed when Cullar D modifications were tested, while Hm1 and Hm2 showed no significant difference in HA uptake and almost constant value after 30 minutes of adsorption. Cm1 and Cm2

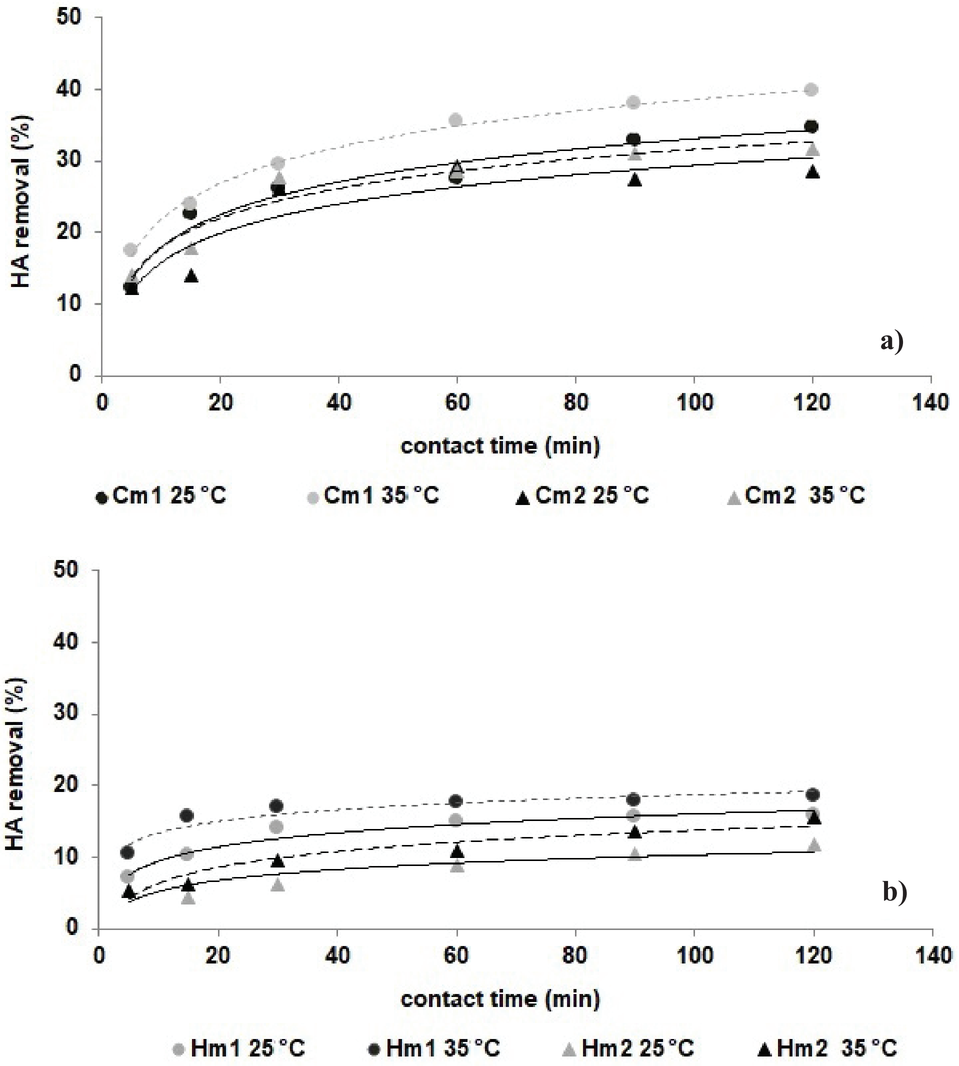

Fig. 6 – *Effects of contact time on HA removal by (a) Cm1 and Cm2, and (b) Hm1 and Hm2 (γ_{HA} = 5 mg L^{-1}, γ_{ads} = 1 g L^{-1}, T = 25 °C and 35 °C, $V_{solution}$ = 100 mL, pH = 7.5, 120 rpm)*

showed a significant initial increase in HA adsorption, which, after 100 minutes approached near equilibrium where curves appear nearly asymptotic to the time axis. The initial significant increase in HA uptake can be attributed to the large number of vacant adsorbent sites, as well as a high solute concentration gradient, but as time passed, the number of vacant adsorbent sites had reduced causing the reduction in HA uptake. After 120 min of adsorption under experimental conditions, Cm1 adsorbed 34.6 % and 39.8 % of HA, while Cm2 adsorbed 28.6 % and 31.7 % of HA at 25 °C and 35 °C, respectively. The Hm1 after 120 minutes removed 15.8 % and 18.6 % of HA at 25 °C and 35 °C, while Hm2 under the same conditions removed only 11.9 % and 15.7 % of HA.

Fig. 6a and 6b also shows the correlation among time needed for equilibrium achievement, adsorption capacity, and effect of modification type on efficiency of HA removal. The similar positive effect of adsorbent modification on HA removal was reported by Pormazar *et al.*[35] who tested humic acid removal using amine-functioned Fe_3O_4 nanoparticles, and Wang *et al.*[32] who tested adsorption of humic acid from aqueous solution onto amino-functionalized degreasing cotton.

Adsorption isotherm models

Adsorption capacity is a key parameter for the application of certain adsorbent in water treatment, while adsorption isotherms are the main tool for prediction of adsorbent feasibility in pollutant removal process and explanation of pollutant accumulation process onto the adsorbent surface at constant temperature. Two non-linear adsorption isotherm models were used to describe the humic acid adsorption onto tested modified activated carbons: Langmuir and Freundlich. The equilibrium

Table 2 – *Langmuir and Freundlich isotherm models for HA adsorption by tested modified activated carbons*

Isotherm	Parameter	25 °C				35 °C			
		Cm1	Cm2	Hm1	Hm2	Cm1	Cm2	Hm1	Hm2
Langmuir	q_m (mg g^{-1})	0.128	0.126	0.105	0.115	0.146	0.129	0.135	0.177
	K_L (L mg^{-1})	1.747	0.572	0.573	0.225	2.797	0.593	0.484	0.144
	r^2	0.967	0.9286	0.953	0.913	0.941	0.814	0.957	0.794
Freundlich	n	2.762	2.030	2.860	1.558	2.883	1.632	2.519	1.395
	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	0.064	0.041	0.042	0.021	0.079	0.040	0.048	0.023
	r^2	0.778	0.872	0.959	0.954	0.748	0.953	0.983	0.952

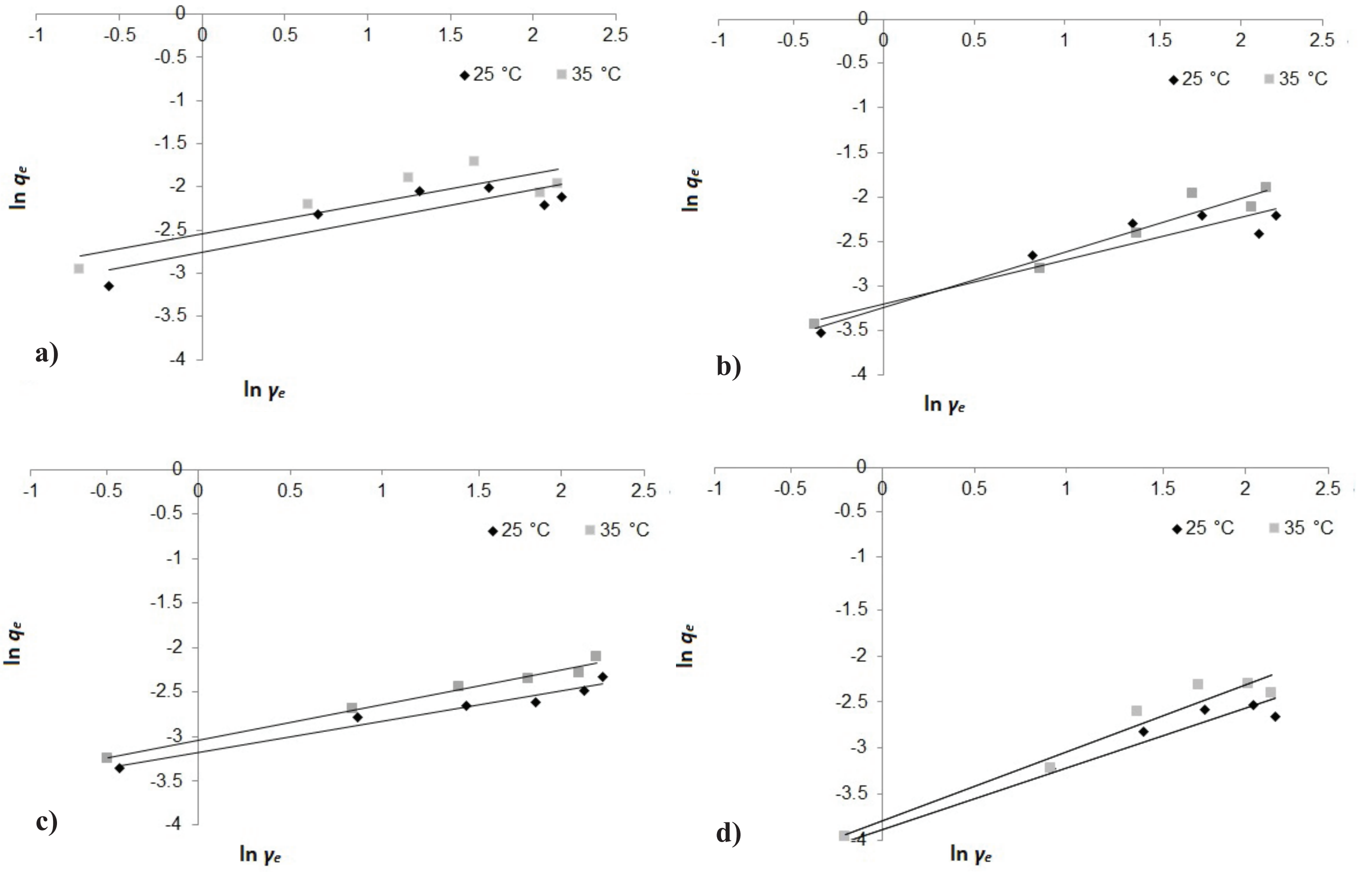

Fig. 7 – *Freundlich isotherms for HA adsorption on (a) Cm1, (b) Cm2, (c) Hm1, and (d) Hm2 (γ_{ads} = 1 g L^{-1}, T = 25 °C and 35 °C, $V_{solution}$ = 100 mL, pH = 7, t = 120 min, 120 rpm)*

adsorption data were processed by adsorption equations at temperatures of 25 °C and 35 °C, and the obtained adsorption parameters for humic acid adsorption onto four adsorbents are presented in Table 2.

The results presented in Table 2 show that both isotherm models represent well the experimental sorption data, since similar range of correlation coefficients (r^2) were obtained. Namely, the r^2 values for Langmuir adsorption model were in the range from 0.913 to 0.967 at 25 °C, and from 0.794 to 0.957 at 35 °C, while the r^2 values of Freundlich adsorption model were in the range from 0.778 to 0.959 at 25 °C, and from 0.748 to 0.983 at 35 °C. However, calculated isotherm parameters revealed that HA adsorption onto Cullar D modifications (Cm1 and Cm2) followed the order: Langmuir > Freundlich, while HA adsorption onto Hydraffin

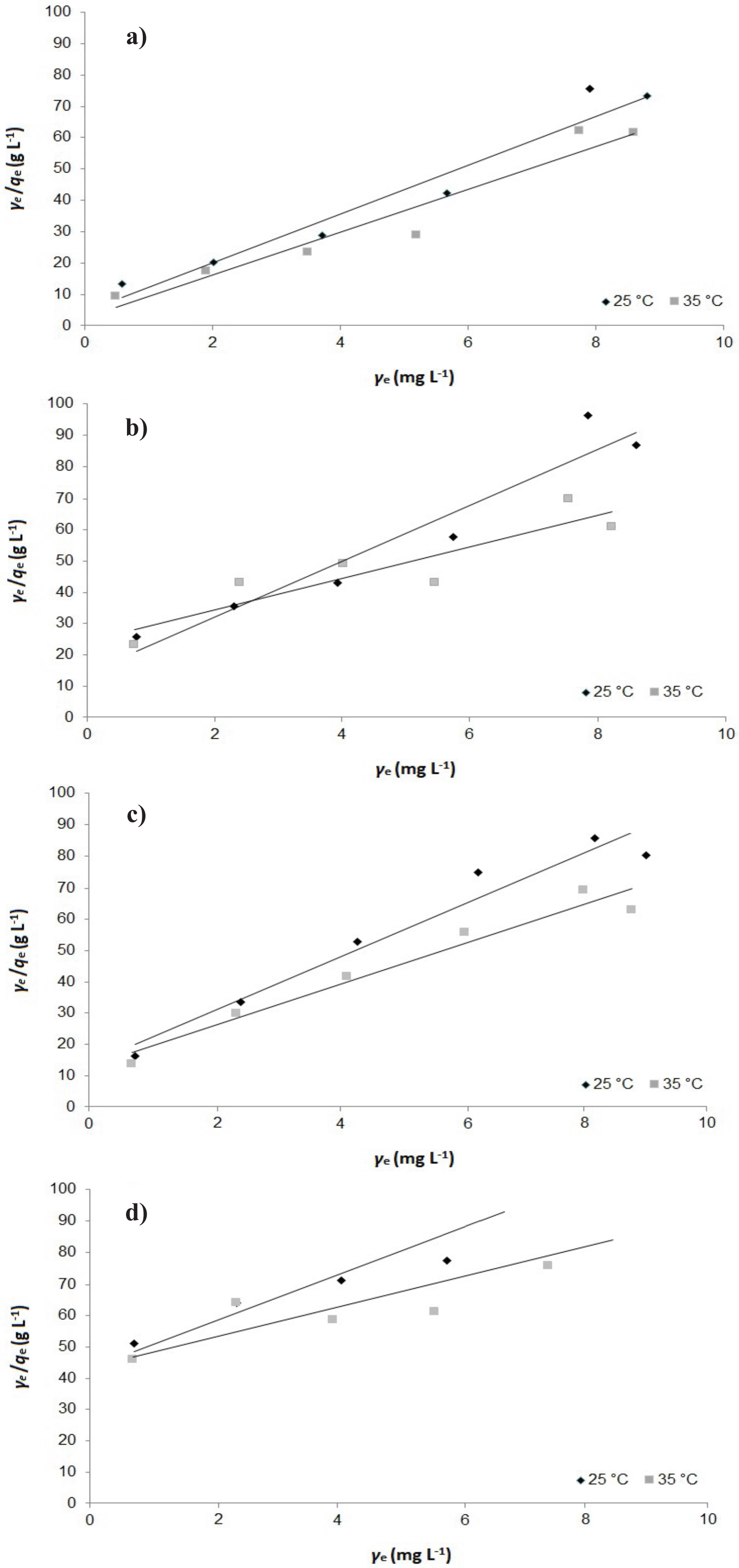

Fig. 8 – *Langmuir isotherms for HA adsorption on (a) Cm1, (b) Cm2, (c) Hm1, and (d) Hm2 (γ_{ads}= 1 g L^{-1}, T= 25 °C and 35 °C, $V_{solution}$ = 100 mL, pH = 7, t = 120 min, 120 rpm)*

30N modifications (Hm1 and Hm2) followed the order: Freundlich > Langmuir. Therefore, HA adsorption onto Cm1 and Cm2 can be characterized as monolayer adsorption, while HA adsorption onto Hm1 and Hm2 can be characterized as multilayer adsorption. Figs. 7 and 8 present Freundlich and Langmuir isotherm modeling for HA adsorption onto Cm1, Cm2, Hm1 and Hm2.

Comparison of the maximum adsorption capacity values according to Langmuir adsorption model confirmed obtained results of this study, i.e., higher adsorption capacities of Cullar D modifications. The maximum adsorption capacities for Cm1 and Cm2 were found to be 0.128 and 0.126 mg g^{-1} at 25 °C, and 0.146 and 0.223 mg g^{-1} at 35 °C, while maximum adsorption capacities for Hm1 and Hm2 were found to be 0.105 and 0.115 mg g^{-1} at 25 °C, and 0.135 and 0.177 mg g^{-1} at 35 °C, respectively.

Comparing the results obtained in this study, it could be observed that the modified adsorbents had a higher adsorption capacity for HA under higher temperature, suggesting that the HA adsorption processes onto Cm1 and Hm1 were exothermic reactions.

The processes of HA adsorption onto Hm2 and Cm2, according to Narbutt[36] could be explained by the hydrophobic effect, i.e., increase in the thermodynamic activity of large hydrophobic molecules formed in metal complexes, which promotes their transfer from the aqueous to the solid (organic) phase. This is unusual behavior for HA-adsorbent system since most of the studies[37,38] have reported decrease in adsorption capacities with increase in temperature and, therefore, further thermodynamic investigations with used modified adsorbents should be conducted.

Conclusions

In the past decade, adsorption, as a water-treatment method, has been in the focus of many studies, primarily due to simplicity of the process and wide range of low-cost materials that can be used as the adsorbents. Furthermore, the significant increase of adsorption capacities have been reported after chemical modification of low-cost materials, especially those conducted in aim of adsorbent iron-coating. Therefore, the purpose of this study was to investigate the efficiency of humic acid removal from water using two commercially available bituminous coal-based activated carbons, Cullar D and Hydraffin 30N. Both activated carbons were modified using following protocols: (1) oxidation by acid mixture (m1), and (2) oxidation with acid mixture followed by Fe^{3+}-ions impregnation (m2).

The efficiency in HA removal from water of each modification was tested by batch adsorption tests under various process parameters: adsorbent mass, initial HA concentration, pH, contact time, and temperature. All tested parameters showed significant influence on HA removal efficiency, i.e., increase in adsorbent mass increased the rate of HA removal, and maximum of HA uptake of 96 % was obtained when Cm1 was used in higher adsorbent mass dose at 35 °C. The maximum uptake of HA by Hm1 was 58.2 %, obtained when the same adsorbent dose was used at the same temperature. After surface coating with Fe-ions (m2), both activated carbons showed similar performances but lower efficiency in HA removal (Cm2 up to 62.1 % and Hm2 up to 50.3 %), which was attributed to thermodynamic activity of large hydrophobic molecules formed in metal complexes.

The results of the tests conducted in order to define the initial HA concentration effect on HA removal showed that adsorption systems HA –Cm1, –Cm2, –Hm1 and –Hm2 are concentration-dependent. The highest removal of HA was achieved using Cm1 at 35 °C and 7 mg L^{-1} of initial HA concentration, while Hydraffin 30N modification Hm1 showed the highest efficiency when initial HA concentration of 10 mg L^{-1} was tested at 35 °C, implying that HA removal was more effective when pH was less than 7, and the highest efficiencies of HA removal were obtained at pH 4.5. Intensive adsorption of HA onto adsorbents surface under acid conditions were attributed to protonated adsorbent surface and fast diffusion of humic acid into adsorbent structure caused by changes in the diffusion properties of HA.

The contact time had different effects on HA adsorption by tested AC's modifications and two phases of adsorption dynamic (fast and slow) were observed as well as their similarities related to AU type. The adsorption system HA and –Hm1 and –Hm2 reached equilibrium almost within the first minutes of adsorption, while the adsorption system HA–Cm1 and HA –Cm2 reached equilibrium almost after 100 minutes suggesting existence of more active sites on Cm1 and Cm2 surface.

The equilibrium data were analyzed using Langmuir and Freundlich equations. Due to obtained results and values of the correlation coefficients (r^2), it could be concluded that Cm1 and Cm2 adsorbed HA in form of monolayer, while HA adsorption onto Hm1 and Hm2 were in the form of multilayer. FTIR analysis confirmed structural changes and mutual difference of chemically modified activated carbons, as well as favorable structure of Cm1 for HA adsorption.

ACKNOWLEDGEMENTS

This work was realized thanks to the Erasmus+ Programme.

References

1. *Singh, R.*, Water and Membrane Treatment in Membrane Technology and Engineering for Water Purification (Second Edition). Application, Systems Design and Operation, 2015, pp. 81–178.
2. *Sillanpää, M.,* Natural Organic Matter in Water: Characterization and Treatment Methods. IWA Publishing, Elsevier, Oxford. 2014.
3. *Bhatnagar, A., Sillanpää, M.*, Removal of natural organic matter (NOM) and its constituents from water by adsorption – A review, Chemosphere **166** (2017) 497. doi: https://doi.org/10.1016/j.chemosphere.2016.09.098
4. *Metcalfe, D., Rockey, C., Jefferson, B., Judd, S., Jarvis, P.*, Removal of disinfection by-product precursors by coagulation and innovative suspended ion exchange process, Water Res. **87** (2015) 20. doi: https://doi.org/10.1016/j.watres.2015.09.003
5. *Santos, A. F., Paiva, P. M., Teixeira, J. A., Brito, A. G., Coelho, L. C., Nogueira, R.,* Coagulant properties of Moringa oleifera protein preparations: Application to humic acid removal, Environ. Technol. **33** (2012) 69. doi: https://doi.org/10.1080/09593330.2010.550323
6. *Sillanpää, M., Ncibi, M. C., Matilainen, A.*, Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review, J. Environ. Manage. **208** (2018) 56. doi: https://doi.org/10.1016/j.jenvman.2017.12.009
7. *Zazouli, M. A., Kalankesh, L. R.*, Removal of precursors and disinfection by-products (DBPs) by membrane filtration from water; A review, J. Environ. Health. Sci. Engineer. **15** (2017) 25. doi: https://doi.org/10.1186/s40201-017-0285-z
8. *Matilainen, A., Vepsalainen, M., Sillanpää, M.,* Natural organic matter removal by coagulation during drinking water treatment: A review, Adv. Colloid Interfac. **159** (2010) 189. doi: https://doi.org/10.1016/j.cis.2010.06.007
9. *Liu, J., Zhao, N., Duan, C., Yue, P., Li, T.*, Removal characteristics of dissolved organic matter and membrane fouling in ultrafiltration and reverse osmosis membrane combined processes treating the secondary effluent of wastewater treatment plant, Water. Sci. Technol. **83** (2021) 689. doi: https://doi.org/10.2166/wst.2020.589
10. *Salvestrini, S., Fenti, A., Chianese, S., Iovino, P., Musmarra, D.*, Electro-oxidation of humic acids using platinum electrodes: An experimental approach and kinetic modelling, Water **12** (2020) 2250. doi: https://doi.org/10.3390/w12082250
11. *Du, X., Li, Z., Xiao, M., Mo, Z., Wang, Z., Li, X., Yang, Y.,* An electro-oxidation reactor for treatment of nanofiltration concentrate towards zero liquid discharge, Sci. Total Environ. **783** (2021) 146990. doi: https://doi.org/10.1016/j.scitotenv.2021.146990
12. *Duan, J., Wilson, F., Graham, N., Tay, J. H.,* Adsorption of humic acid by powdered activated carbon in saline water conditions, Desalination **151** (2002) 53. doi: https://doi.org/10.1016/S0011-9164(02)00972-4
13. *Islam, M. A., Morton, D. W., Johnson, B. B., Angove, M. J.,* Adsorption of humic and fulvic acids onto a range of adsorbents in aqueous systems, and their effect on the adsorption of other species: A review, Sep. Purif. Technol. **247** (2020) 116949. doi: https://doi.org/10.1016/j.seppur.2020.116949
14. *Feng, J., Xing, B., Chen, H.,* Catalytic ozonation of humic acid in water with modified activated carbon: Enhancement and restoration of the activity of an activated carbon catalyst, J. Environ. Manage. **237** (2019) 114. doi: https://doi.org/10.1016/j.jenvman.2019.02.061
15. *Jada, A., Akbour, R. A., Douch, J.,* Surface charge and adsorption from water onto quartz sand of humic acid, Chemosphere **64** (2006) 1287. doi: https://doi.org/10.1016/j.chemosphere.2005.12.063
16. *Abouleish, M. Y. Z., Wells, M. J. M.,* Trihalomethane formation potential of aquatic and terrestrial fulvic and humic acids: Sorption on activated carbon, Sci. Tot. Environ. **521–522** (2015) 393. doi: https://doi.org/10.1016/j.scitotenv.2015.03.090
17. *Su, X., Hu, J., Zhang, J., Liu, H., Yan, C., Xu, J., Ma, Y., Song, J.*, Investigating the adsorption behavior and mechanisms of insoluble Humic acid/starch composite microspheres for metal ions from water, Colloid. Surfaces A **610** (2021) 125672. doi: https://doi.org/10.1016/j.colsurfa.2020.125672
18. *Barhoumi, A., Ncib, S., Chibani, A., Brahmi, K., Bouguerra, W., Elaloui*, *E.,* High-rate humic acid removal from cellulose and paper industry wastewater by combining electrocoagulation process with adsorption onto granular activated carbon, Ind. Crops. Prod. **140** (2019) 111715. doi: https://doi.org/10.1016/j.indcrop.2019.111715
19. *Kitis, M., Kaplan, S. S., Karakaya, E., Yigit, N. O.*, Civelekoglu, *G.,* Adsorption of natural organic matter from waters by iron coated pumice, Chemosphere **66** (2007) 130. doi: https://doi.org/10.1016/j.chemosphere.2006.05.002
20. *Ding, D., Yang, X., Lui, W., Chang, Y., Shang, C.*, Removal of natural organic matter using surfactant-modified iron oxide-coated sand, J. Hazard. Mater. **174** (2010) 567. doi: https://doi.org/10.1016/j.jhazmat.2009.09.089
21. *Noorimotlagh, Z., Ravanbakhsh, M., Valizadeh, M. R., Kyzas, G. Z., Ahmafi, M., Rahbar, N., Jaafarzadeh, N.,* Optimization and genetic programming modeling of humic acid adsorption onto prepared activated carbon and modified by multi-wall carbon nanotubes, Polyhedron **179** (2020) 114354. doi: https://doi.org/10.1016/j.poly.2020.114354
22. *Hongxia, Z., Xiaoyun, W., Honghong, L., Tianshe, T., Wangsuo, W., Zhou, Y., Zhang, Y., Li, P., Li, G., Jiang, T.,* Adsorption behavior of Th(IV) onto illite: Effect of contact time, pH value, ionic strength, humic acid and temperature, Powder Technol. **251** (2014) 1. doi: https://doi.org/10.1016/j.clay.2016.03.038
23. *Habuda-Stanić, M., Kalajdžić, B., Kuleš, M., Velić, N.,* Arsenite and arsenate sorption by hydrous ferric oxide/polymeric material, Desalination **229** (2008) 1. doi: https://doi.org/10.1016/j.desal.2007.06.034
24. *Sepehr, M. N., Sivasankar, V., Zarrabi, M., Kumar, M. S.,* Surface modification of pumice enhancing its fluoride adsorption capacity: An insight into kinetic and thermodynamic studies, Chem. Eng. J. **228** (2013) 192. doi: https://doi.org/10.1016/j.cej.2013.04.089
25. *Dalifullah, A. A. M., Yakout, S. M., Elreefy, S. A.,* Adsorption of fluoride in aqueous solutions using $KMnO_4$ – modified activated carbon derived from steam pyrolysis of rice straw, J. Hazard. Mater. **147** (2007) 633. doi: https://doi.org/10.1016/j.jhazmat.2007.01.062
26. *Zolfaghari, G., Esmaili-Sari, A., Younesi, H., Baydokhti, R. R.,* Surface modification of ordered nanoporous carbons CMK-3 via a chemical oxidation approach and its application in removal of lead pollution from water, in Proceedings of the 2nd International Conference on Environmental Science and Technology, IPCBEE, vol. 6, Singapore, 2011. pp. 174–178.

27. *Yang, J., Zhao, Y., Ma, S., Zhu, B., Zhang, J., Zheng, C.,* Mercury removal by magnetic biochar derived from simultaneous activation and magnetization of sawdust, Environ. Sci. Technol. **50** (2016) 12040.
doi: https://doi.org/10.1021/acs.est.6b03743
28. *Stjepanović, M., Velić, N., Lončarić, A., Gašo-Sokač, D., Bušić, V., Habuda-Stanić, M.,* Adsorptive removal of nitrate from wastewater using modified lignocellulosic waste material, J. Mol. Liq. **285** (2019) 535.
doi: https://doi.org/10.1016/j.molliq.2019.04.105
29. *Gil, A., Taoufik, N., García, A. M., Korili, S. A.*, Comparative removal of emerging contaminants from aqueous solution by adsorption on an activated carbon, Environ. Technol. **40** (2019) 3017.
doi: https://doi.org/10.1080/09593330.2018.1464066
30. *Menéndez, J., Illán-Gómez, M., Leon, C., Radovic, L.,* On the difference between the isoelectric point and the point of zero charge of carbons, Carbon **33** (1995) 1655.
31. *Bernal, V., Erto, A., Giraldo, L., Moreno-Piraján, J. C.,* Effect of solution pH on the adsorption of paracetamol on chemically modified activated carbons, Molecules **22** (2017) 1032.
doi: https://doi.org/10.3390/molecules22071032
32. *Li, C., Dong, Y., Wu, D., Peng, L., Kong, H.*, Surfactant modified zeolite as adsorbent for removal of humic acid from water, Appl. Clay Sci. **52** (2011) 353.
doi: https://doi.org/10.1016/j.clay.2011.03.015
33. *Baek, M.-H., Ijagbemi, C. O., O, S. J., Kim, D. S.,* Removal of malachite green from aqueous solution using degreased coffee bean, J. Hazard. Mater. **176** (2010) 820.
doi: https://doi.org/10.1016/j.jhazmat.2009.11.110
34. *Soleimani, H., Mahvi, A. H., Yaghmaeian, K., Abbasnia, A., Sharafi, K., Mahmood Alimohammadi, M., Zamanzadeh, M.*, Effect of modification by five different acids on pumice stone as natural and low-cost adsorbent for removal of humic acid from aqueous solutions – Application of response surface methodology, J. Mol. Liq. **290** (2019) 111181.
doi: https://doi.org/10.1016/j.molliq.2019.111181
35. *Pormazar, S. M., Ehrampoush, M. H., Ghaneian, M. T.,* Application of amine-functioned Fe_3O_4 nanoparticles with HPEI for effective humic acid removal from aqueous solution: Modeling and optimization, Korean J. Chem. Eng. **37** (2020) 93.
doi: https://doi.org/10.1007/s11814-019-0411-y
36. *Narbutt, J.,* Fundamentals of Solvent Extraction of Metal Ions – Liquid-Phase Extraction, Elsevier, 2020.
doi: https://doi.org/10.1016/B978-0-12-816911-7.00004-9
37. *Naghizadeh, A., Kamranifar, M., Yari, A. R., Mohammadi, M. J.,* Equilibrium and kinetics study of reactive dyes removal from aqueous solutions by bentonite nanoparticles. Desalin. Water Treat. **97** (2017) 329.
doi: https://doi.org/10.5004/dwt.2017.21687
38. *Derakshani, E., Naghizadeh, A.,* Optimization of humic acid removal by adsorption onto bentonite and montmorillonite nanoparticles, J. Mol. Liq. **259** (2018) 76.
doi: https://doi.org/10.1016/j.molliq.2018.03.014