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Adsorption of Diclofenac onto Activated Carbons

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Abstract

The presence of pharmaceuticals in natural waters has been the subject of numerous studies in the last decade due to their potential negative effects on human health and the environment. Indeed, the intensive use of pharmaceuticals leads to their presence in municipal wastewater. Unfortunately, international and national regulations still do not require continuous monitoring of the presence of pharmaceuticals in natural waters and drinking water, so wastewater treatment plants do not focus on removing them from wastewater. Diclofenac, 2-[2-(2,6-dichloroanilino)phenyl]acetic acid (DCF), is a nonsteroidal compound used as an analgesic, anti-inflammatory, and antipyretic drug and is therefore commonly found in wastewater. Due to its properties, DCF remains biologically active in the aquatic environment and easily enters the food chain. Therefore, DCF should be removed from wastewater before it is discharged into water bodies. Adsorption is an efficient and simple method that can be used to remove DCF from water. In this study, the possibility of removing DCF by adsorption on activated carbon is investigated. Modified hazelnut shell (MHS), modified commercial activated carbon Cullar (MC) and unmodified commercial activated carbon Cullar (C) were batch tested as adsorbents. The tested adsorbents were characterised by FTIR, zeta potential and $\mathrm{pH_{pzc}}$, while the adsorbent efficiency was tested in the pH range from 2 to 10 and described by isothermal studies. Among the tested adsorbents, the maximum uptake of 48.7 $\mathrm{mg\,g^{-1}}$ was found when modified activated carbon Cullar was used, while both Freundlich and Langmuir isotherm models fitted well to the data. Modified activated carbon from hazelnut shells showed effective removal of DCF.

Keywords

Activated carbon, diclofenac, adsorption, water

1 Introduction

In addition to common pollutants that can be found in nature, such as pesticides, polycyclic aromatic hydrocarbons, and other contaminants, there are also various types of synthetic or natural chemicals in low concentrations with a high potential of causing known or less known harmful effects on the environment and human health. Precisely, such compounds in today's modern society are produced all over the world in large quantities, and among them are also pharmaceutical products, which are a large and diverse group of compounds designed for the prevention and treatment of diseases, and improvement of health.[1,2]

The increasing development of the pharmaceutical industry has led to an increase in the concentration of various pharmaceuticals in the environment, including water.

Current water treatment plants cannot completely remove pharmaceuticals, resulting in their increased presence in nature. The presence of pharmaceuticals in nature, especially in high concentrations, can lead to long-term damage to health.[3]

Pharmaceuticals can be detected in natural water within concentrations ranging from $\mathrm{\mu g\,l^{-1}}$ to $\mathrm{mg\,l^{-1}}$, but can still cause the formation and spread of new strains of resistant bacteria, leading to problems in their removal.

Diclofenac (DCF) belongs to the very often used group of non-steroidal and anti-inflammatory drugs (NSAID).[4] Due to its biological activity, DCF has a significant impact on the aquatic environment and easily enters the food chain.

In order to reduce the presence of pharmaceutical agents such as DCF in water, numerous methods are used, among which stand out ozonation, membrane filtration and biodegradation, whose application has proven to be effective but expensive. One of the methods that meets both criteria is the adsorption method.[5] In recent years, many studies have investigated the possibility of applying agri-food wastes/by-products as they are available and inexpensive. From the economic point of view, adsorbents should be highly selective for pollutants, efficient and inexpensive.[6] Therefore, the adsorption properties of various carbon-rich agro-industrial waste materials have been investigated in numerous studies.[7] In most of these studies, researchers also investigated the effect of materials' surface modification in order to enlarge adsorption capacity or improve adsorbent selectivity. With this in mind, this research attempted to test the effectiveness of DCF removal using adsorbents derived from modified hazelnut shells, granular bitumen-based commercial activated carbon Cullar, and modified commercial activated carbon Cullar. The use of hazelnut shells (HS) as adsorbents in water treatment can also be used for the simultaneous management of industrial waste as a water treatment option.

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2 Materials and methods

2.1 Adsorbent preparation

The hazelnut shells were kindly provided by PP Orahovica d. o. o., Croatia. A laboratory knife mill (1 mm sieve) MF10 basic (IKA Labortechnik, Germany) was used to grind the material. An amount of 50 g of HS was carbonised at 200 °C for 1 h in a muffle furnace (Nabertherm LE 14/11/R7, Germany) in order to produce charcoal. Since, in preliminary study (results not shown), the HS in native form was unsuccessful in removing DCF from aqueous solutions, a chemical modification of HS was performed in order to improve the materials' surface. Thus, all experiments were performed with modified HS (MHS).

Chemical activation of HS was performed with 98 % sulphuric acid (Carlo Erba Reagents, Italy) in ratio 1 : 1 during 24 h, after which the residual chemicals were washed with demineralised water until neutral pH was reached. Such prepared adsorbent MHS, was oven-dried at 105 °C to a constant mass. The process of activation with sulphuric acid leads to carboxylation and sulphonation, where COOH or CO_2 groups are obtained by oxidation of C−C bonds, and other functional groups, respectively.

The commercially available activated carbon, Cullar D, was provided by Culligan Italiana S.p.A. (Cadriano, Italy). Cullar D was tested in its unmodified form (C), and in modified form (MC). The modification of activated carbon Cullar was performed with 98 % sulphuric acid in ratio 1 : 1, which was described earlier.

2.2 Adsorbent characterisation

Identification of functional groups and adsorbents surface characteristics were determined by FTIR analysis (Cary 630, Agilent Technologies, USA).

The point of zero charges and zeta potential were determined according to *Karthikeyan et al.*[8] – in a series of Erlenmeyer flasks, 50 mg of each adsorbent (MHS, C and MC, respectively), was reacted with 100 ml demineralised water. Suspension pH (range 2–10) was adjusted using 0.1 NaOH or 0.1 HCl. After pH adjustment, the prepared sets were shaken in a thermostatic shaker at 130 rpm at 25 °C for 24 h. The suspension was filtered through filter paper (Whatman). The final pH was then determined for each solution, and the difference between the initial and final pH (ΔpH) was calculated. The pH_{pzc} value was determined using the ΔpH *vs*. $pH_{initial}$ plot. Zeta potential was measured with a Zetasizer (Zetasizer 2000, Malvern Instruments, UK).

2.3 Adsorption experiments

DCF in form of diclofenac sodium ($C_{14}H_{10}Cl_2NNaO_2$), produced by Sigma Aldrich (Germany), was used for the preparation of the DCF stock solution. The DCF stock solution was prepared using 0.1 g of diclofenac sodium in 1 l of demineralised water. The batch tests were conducted in order to define the relationship between DCF removal and the following process parameters: pH value, adsorbent mass, contact time, and initial DCF concentration. The adsorption capacities were investigated in a thermostatic water bath (Bioblock Scientific, Poly-test 20, UK) under 130 rpm for a predetermined time (5–1440 min) at 25 °C. The stock solution was diluted up to the defined initial DCF concentrations in the range of 10 to 50 mg l^{-1}. The adsorbents (MHS, C and MC) were weighed with a laboratory scale (AW 220 M, Shimadzu, Japan). The mass of adsorbents ranged from 0.05 to 0.5 g, and were added to 50 ml 30 mg l^{-1} DCF solution. Desirable initial pH was obtained using NaOH or HCl to obtain pH-values of 2, 4, 6, 8, and 10, and were measured with a pH meter (Seven Easy, Mettler Toledo, Switzerland). Samples were shaken within predetermined time intervals, and then filtered through filter paper (Whatman). The residual concentration of DCF was determined by UV/Vis spectrophotometer (Specord 200, Analytic Jena, Germany) at 276 nm using 10 mm and 50 mm quartz cells. Average results obtained by duplicate sets are reported, and were used for further calculations.

The percentage of DCF removal (*R*, %) was calculated as follows:

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

where γ_0 is the initial DCF concentration (mg l^{-1}) and γ is the residual DCF concentration (mg l^{-1}).

The amount of DCF adsorbed onto MHS, q_e (mg g^{-1}), C and MC at equilibrium was calculated as follows:

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

where γ_e (mg l^{-1}) is the concentration of DCF at equilibrium, *V* is the volume of solution (l), and *m* (g) is the mass of MHS, C or MC.

3 Results and discussion

3.1 Characterisation of adsorbents

The functional groups of the used adsorbents were identified using FTIR spectroscopy, and obtained spectra are shown in Fig. 1.

Presented FTIR spectra show a broad band at 3272, 3287, and 3250 cm^{-1} which were assigned to O−H stretching vibrations caused by intramolecular bonding of polymeric compounds, such as alcohol, phenol, and carboxylic acid, indicating the presence of free hydroxyl groups at the adsorbents surface.[9] The presence of these oxygen complexes may add a polar nature to activated carbons (*i.e.*, hydrophilicity and acidity to the carbon surface).[10] The band at 2922.2 cm^{-1} was assigned to C−H stretching vibration in the CH_2 group. The adsorption peaks at 1625, 1647, and 1640 cm^{-1} are from C=C stretching vibrations at the aromatic ring, which can be found in carbonaceous ma-

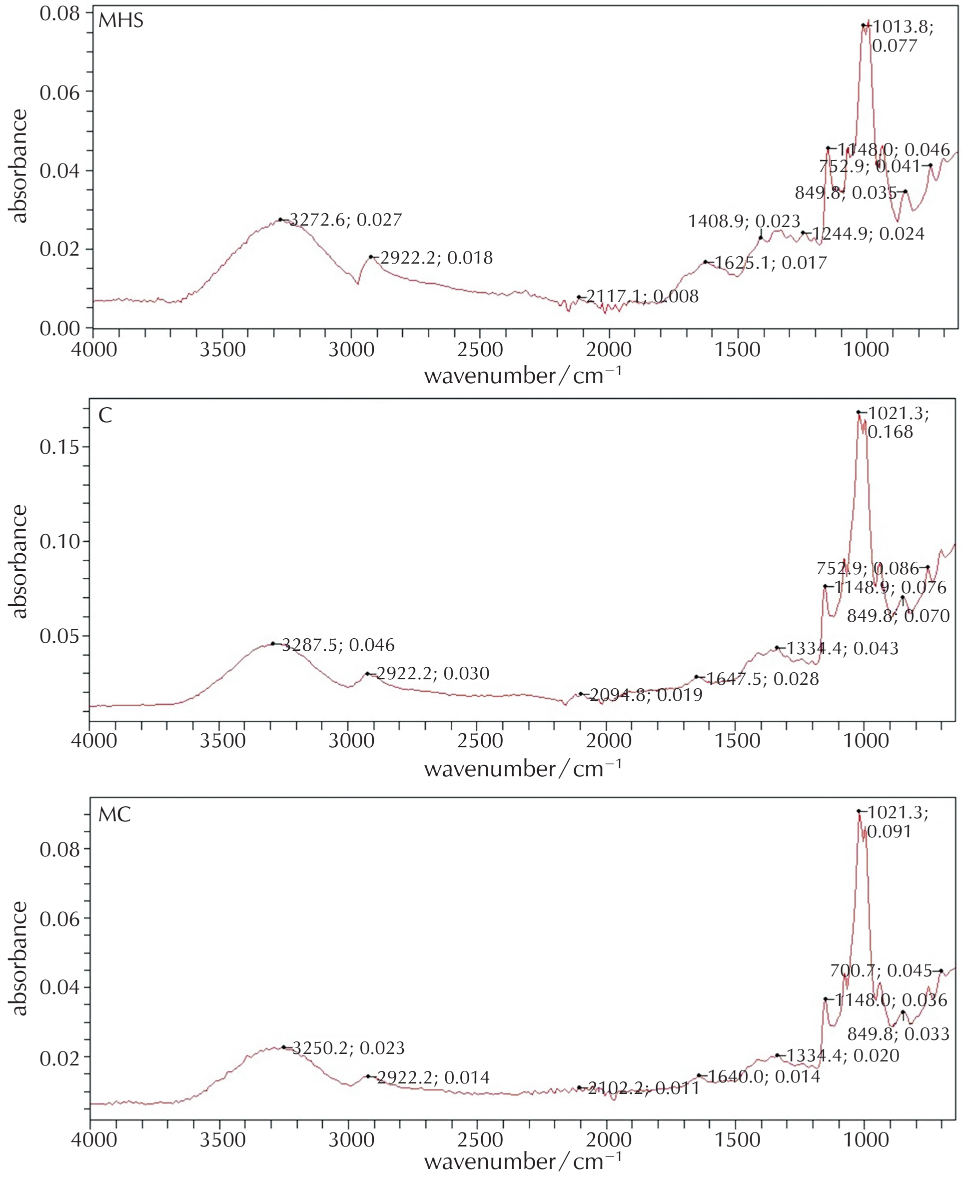

Fig. 1 – FTIR spectra of MHS, C and MC
Slika 1 – FTIR spektri za MHS, C i MC

terials such as activated carbon.[11] Sharp peaks at 1000–1700 cm^{-1} were assigned to C=O and COOH groups. The formation of hydrogen bonds between phenol groups and diclofenac sodium on the surface of activated carbons could be crucial in the adsorption process.[12]

The point of zero adsorbent charge (pH$_{pzc}$) presents the pH at which the adsorbent's surface charge is zero. The value of pH$_{pzc}$ depends on the number of H$^+$ or OH$^-$ ions present in the treated solution, and can change the potential surface charge of adsorbents. A lower value of pH than pH$_{pzc}$ will cause protonation of the adsorbent's surface functional groups, while pH above pH$_{pzc}$, will deprotonate the surface due to the presence of OH$^-$ ions in the solution.[13] In short, the point of zero charge corresponds to a pH at which the surface charge of the adsorbent is equal to zero. Determining the point of zero charge contributes to clearer understand of the electrostatic interactions among the adsorbent surface and the adsorbate at a given pH value.[14,15] Fig. 2 shows that pH$_{pzc}$ for MHS is 4.9, for C 6.4, and for MC 3. If the final pH is lower than pH$_{pzc}$, the adsorbent surface is positively charged and the process conditions are suitable for anion adsorption. If pH > pH$_{pzc}$, the surface of the adsorbent is negatively charged and suitable for cation adsorption.[15] MHS has a negative zeta potential in the pH range from 7 to 10, C in the pH range from 6 to 10, while MC from 4 to 10, corresponding to their surface charges.

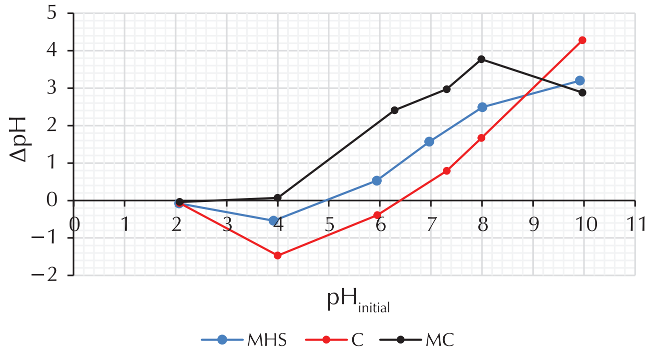

Fig. 2 – Determination of pH value of point of zero charge (pH_{pzc}) for MHS, C, and MC

Slika 2 – Određivanje pH vrijednosti točke nultog naboja (pH_{pzc}) za MHS, C i MC

3.2 Effect of contact time

The contact time has a strong effect on each adsorption process. From Fig. 3 it is visible that the DCF removal increases with contact time, and the maximum removals (92, 100, and 97 % for MHS, C and MC, respectively) were obtained after 360, *i.e.,* 240 min. The amount of adsorbed DCF also increases proportionally with time, and the maximum calculated values were 4.87, 5.31, and 5.26 $mg\,g^{-1}$ for MHS, C, and MC, respectively. Fig. 3 also shows that an increase in time from 240 min onwards does not result in a higher percentage of DCF removal. The equilibrium for MC was reached after 60 min. The obtained results coincide with the research of *Jodeh et al.*[16], where the adsorbed amount of DCF and amoxicillin increased with contact time, and the adsorption capacity for DCF showed a rapid increase in adsorption during the first 30 min.

3.3 Effect of adsorbent concentration

The material's adsorption behaviour is determined by the type of surface's active groups, as well as adsorbent concentration.[17] An increase in adsorbent concentration implies an increase in free sites for adsorbate binding. However, research has proven that adsorption of pharmaceuticals rarely reaches a saturation value. Therefore, further increase in adsorbent concentration is not of great importance.[18]

Fig. 4 shows that the percentage of DCF removal also increases with adsorbent mass up to 6 $g\,l^{-1}$, and the amount of adsorbed DCF was 4.75 $mg\,g^{-1}$. Each further increase in adsorbent mass does not contribute to a higher percentage of DCF removal, and the maximum value was 89 % for MHS. A similar trend was observed with activated carbon Cullar (Fig. 4), but at lower mass concentrations of the adsorbent, higher percentages of DCF removal were

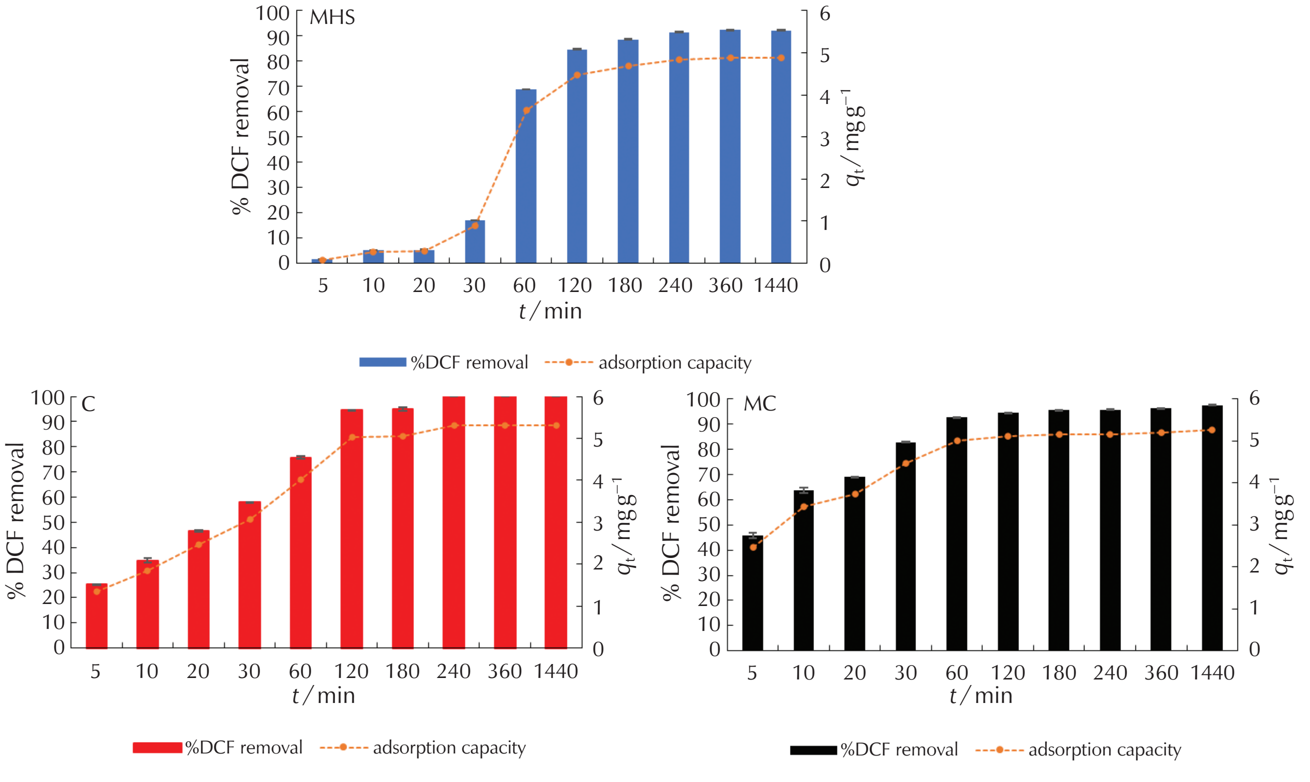

Fig. 3 – Relationship between contact time and removal of DCF (%) using MHS, C, and MC (γ_{DCF} = 30 $mg\,l^{-1}$, $m_{adsorbent}$ = 0.3 g, $V_{solution}$ = 50 ml, pH = 5.3, t = 120 min, T = 25 °C, 130 revolutions *per* minute)

Slika 3 – Utjecaj vremena na učinak uklanjanja DCF-a (%) primjenom MHS-a, C-a i MC-a (γ_{DCF} = 30 $mg\,l^{-1}$, $m_{adsorbens}$ = 0,3 g, $V_{otopine}$ = 50 ml, pH = 5,3, t = 120 min, T = 25 °C, 130 okretaja u minuti)

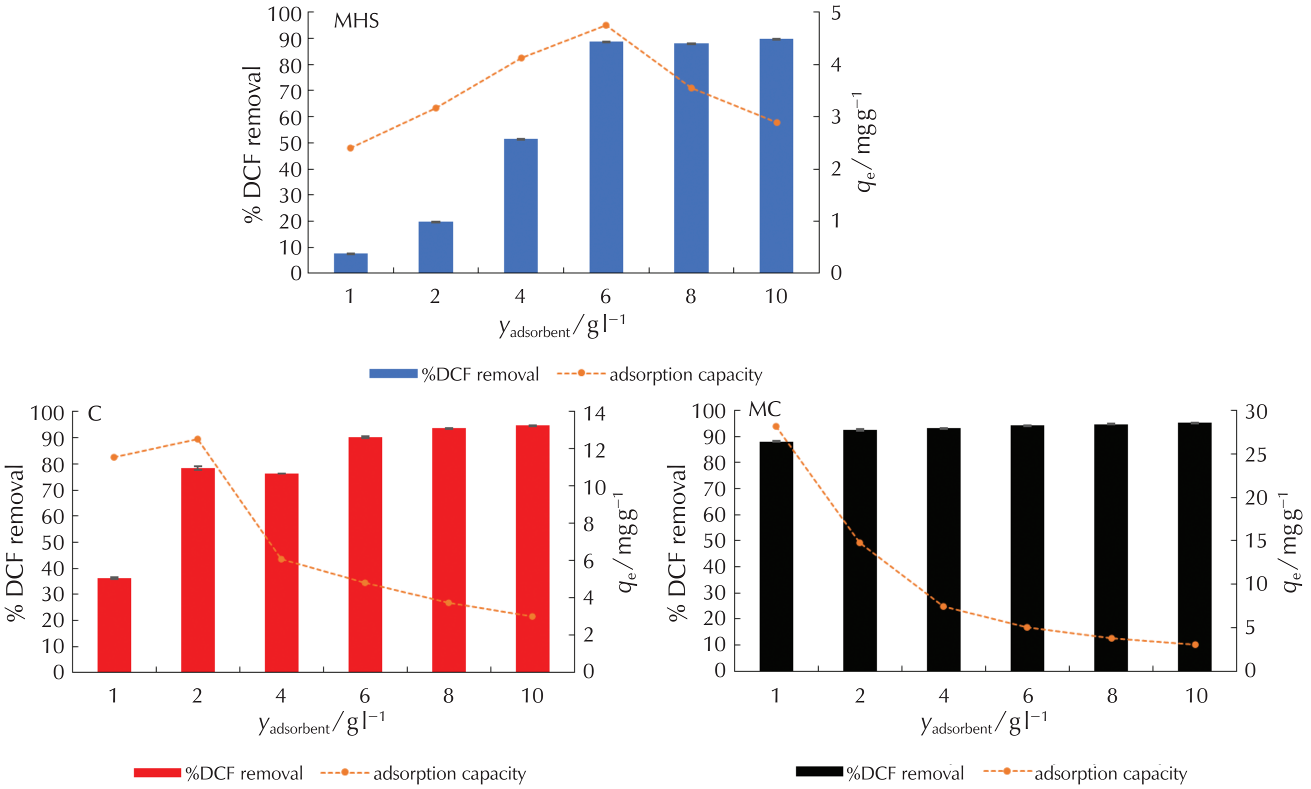

Fig. 4 – Relationship between the adsorbent concentration and DCF removal (%) using MHS, C, and MC (γ_{DCF} = 30 mg l^{-1}, $V_{solution}$ = 50 mL, pH = 5.3, t = 120 min, T = 25 °C, 130 revolutions *per* minute)

Slika 4 – Utjecaj početne masene koncentracije na učinak uklanjanja DCF-a (%) primjenom MHS-a, C-a i MC-a (γ_{DCF} = 30 mg l^{-1}, $V_{otopine}$ = 50 mL, pH = 5,3, t = 120 min, T = 25 °C, 130 okretaja u minuti)

achieved, and the amount of adsorbed DCF was reached at 4 g l^{-1} of the adsorbent, after which the adsorbed amount of DCF decreased. As expected, the lowest percentage of DCF removal was at the lowest mass concentration (1 g l^{-1}) and was 88 %. Accordingly, an increase in the mass concentration of the adsorbent decreased the adsorbed amount of DCF.

The obtained results are similar to the research conducted by *Kim and Tanaka*[19] in which they proved that the adsorption of trimethoprim at an adsorbent mass of 1 g l^{-1} reached the saturation value on activated carbon, and a further increase in mass had not lead to an increase in adsorption capacity. Considering the results obtained, attention should be paid to the optimal mass of adsorbent that maximally removes DCF from wastewater in order to rationally use resources and obtain the best possible results, as well as to reduce the overall cost of the process.[19] Since the relationship between the percentage of DCF removal and adsorption capacity was most favourable at 6 g l^{-1} adsorbent, the specified mass was used for further studies.

3.3 Effect of initial diclofenac concentration

Fig. 5 shows the relation between the amount of adsorbed DCF and its initial concentrations for tested materials. Total DCF removal (100 %) was achieved with C and MC when initial DCF concentration was 10 mg l^{-1}. The amount of adsorbed DCF by MHS increased from 1.12 mg g^{-1} (γ_{DCF} = 10 mg l^{-1}) to 7.98 mg g^{-1} (γ_{DCF} = 50 mg l^{-1}). By applying activated carbon Cullar, the adsorbed amount of DCF increased from the initial 1.57 mg g^{-1} to 7.28 mg g^{-1}, and with MC from 1.72 to 8.46 mg g^{-1}, which suggests

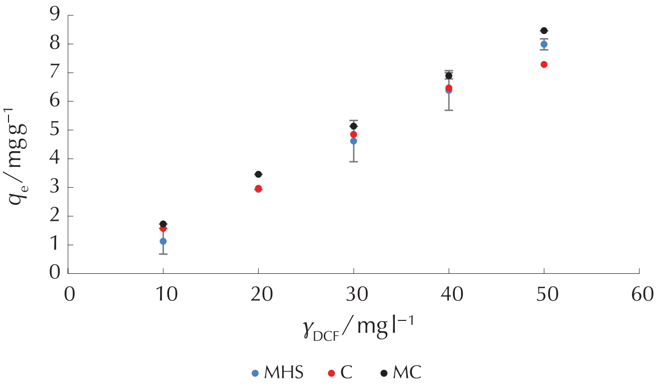

Fig. 5 – Relationship between the initial DCF concentration and DCF adsorption onto MHS, C, and MC ($\gamma_{adsorbent}$ = 6 g l^{-1}, $V_{solution}$ = 50 ml, pH = 5.3, t = 120 min, T = 25 °C, 130 revolutions *per* minute)

Slika 5 – Utjecaj početne masene koncentracije DCF-a na adsorpciju DCF-a primjenom MHS-a, C-a i MC-a ($\gamma_{adsorbens}$ = 6 g l^{-1}, $V_{otopine}$ = 50 ml, pH = 5,3, t = 120 min, T = 25 °C, 130 okretaja u minuti) that the adsorbed amounts of DCF by C and MC were approximately equal. According *Aksu and Tunç*,[20] adsorption capacity increment of tested adsorbents (activated carbon, activated sludge and *Rhizopus arrhizus*) is caused by the increment of initial pharmaceutical concentration. *Li et al.*[21] tested the removal of tetracycline by activated carbon and reported an increase in adsorption capacity of more than twofold with increasing tetracycline concentration.

3.4 Effect of pH

Fig. 6 shows the relationship between initial pH and DCF removal (%) using tested adsorbents MHS, C, and MC. The exact mechanism of adsorption is a very complex process, and it depends on several factors. The pH value has great importance on the adsorption of pharmaceuticals. Protonation or deprotonation of ionising pharmaceutical products changes their physicochemical properties, and thus their tendency towards adsorption.[22] A change in the charge of the molecule, changes the amount of adsorbed pharmaceutical. This has been proven and reported by *Moussavi et al*.[23], who tested amoxicillin removal by activated carbon – the percentage of removal increased at pH values of 5 and 6, while it decreased at acidic and alkaline pH values. The molecule of DCF contains several groups (*i.e.,* chlorine, carboxyl, benzene, and imine groups). The presence of carboxyl groups means that DCF molecules are negatively charged in water. This means that electrostatic interaction is most likely between positively charged adsorbents and DCF molecules. However, the presence of aromatic rings in the DCF molecules suggests that π-π stacking and hydrophobic interactions can also enhance the adsorption of DCF.[24]

This research showed that activated carbons modified with H_2SO_4 had a high percentage of removal (over 90 %) at all pH values. The percentage of DCF removal with activated carbon Cullar increased with the alkalinity of the solution, while in acidic conditions, no adsorption occurred at all.

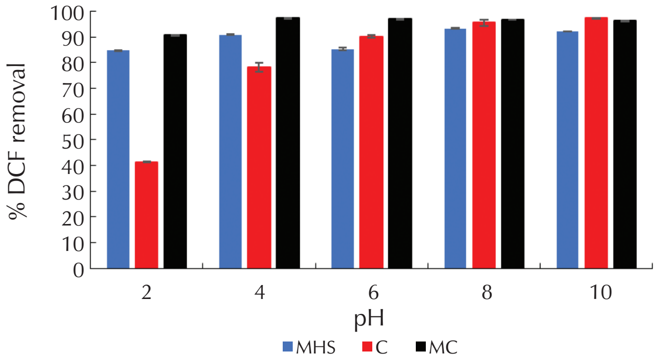

Fig. 6 – Relationship between initial pH and DCF removal (%) using MHS, C, and MC (γ_{DCF} = 30 mg l^{-1}, $\gamma_{adsorbent}$ = 6 g l^{-1}, $V_{solution}$ = 50 ml, t = 120 min, T = 25 °C, 130 revolutions *per* minute)

Slika 6 – Utjecaj početnog pH na uklanjanje DCF-a (%) primjenom MHS-a, C-a i MC-a (γ_{DCF} = 30 mg l^{-1}, $\gamma_{adsorbens}$ = 6 g l^{-1}, $V_{otopine}$ = 50 ml, t = 120 min, T = 25 °C, 130 okretaja u minuti)

It can be concluded that the influence of pH in different types of pharmaceuticals works differently depending on the functional groups on a certain pharmaceutical product, but also on the behaviour of activated carbon at high and low pH values.[18]

3.5 Adsorption isotherms

The data analyses were performed by the non-linearised Langmuir and Freundlich isotherms. The Freundlich adsorption isotherm (Eq. (3)) is used to describe multilayer heterogeneous adsorption on adsorbent surfaces.

$$q_e = K_F \cdot \gamma_e^{1/n} \tag{3}$$

K_F is the Freundlich constant, which refers to the adsorption capacity, and n describes the intensity of adsorption. If $n < 1$, it means that adsorption is a chemical process, if $n = 1$, adsorption is linear, and if $n > 1$, adsorption is a physical process. The values of the constant n in this research were 0.879 (MHS), 1.096 (C), and 1.009 (MC). According to these data, the adsorption of DCF on MHS is a chemical process, while the adsorption on C and MC is a physical process.

Adsorption in a monomolecular layer is described by the Langmuir adsorption isotherm (Eq. (4)).

$$q_e = \frac{q_m \cdot K_L \cdot \gamma_e}{1 + K_L \cdot \gamma_e} \tag{4}$$

where q_m (mg g^{-1}) is the adsorption capacity, and K_L (l mg^{-1}) is the Langmuir constant. The dimensionless parameter R_L shows whether the adsorption is favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The above is calculated according to Eq. (5).

$$R_L = \frac{1}{1 + K_L \cdot \gamma_0} \tag{5}$$

where γ_0 (mg l^{-1}) is the highest initial concentration of DCF.

The R_L values shown in Table 1 were 0.991 (MHS), 0.732 (C), and 0.667 (MC), suggesting that the adsorption of DCF on adsorbents under the given experimental conditions was a favourable process.

By analysing the coefficients of determination, R^2, it seems that both models describe the experimentally obtained data well. The obtained results (MHS, C, and MC adsorption capacities for DCF) were compared with the adsorption capacities of others studies: 126 mg g^{-1} was achieved with activated carbon made from argan shells,[25] 405 mg g^{-1} with coconut activated carbon,[26] and 166,67 mg g^{-1}.[27]

4 Conclusion

The adsorption of DCF onto MHS, C, and MC was investigated. The modification of hazelnut shells yielded more functional groups, thus, facilitating DCF removal from

Table 1 – Isotherm parameters for the DCF adsorption onto MHS, C, and MC
Tablica 1 – Parametri izotermi adsorpcije DCF-a na MHS-u, C-u i MC-u

Isotherm	MHS	C	MC
Freundlich			
K_F / mg g^{-1} (mg l^{-1})$^{1/n}$	0.090	0.207	0.170
n	0.879	1.096	1.009
R^2	0.998	0.996	0.999
Langmuir			
$q_{m,cal}$ / mg g^{-1}	8.550	9.871	8.45
K_L / l mg^{-1}	0.001	0.037	0.059
R_L	0.991	0.732	0.667
R^2	0.998	0.997	0.999

aqueous solution. Although the commercial activated carbon, Cullar, was efficient in removing DCF, its modified version, MC, showed an even higher percent removal of DCF as well as a higher adsorption capacity. The equilibrium data of the systems studied fitted well with the models of Langmuir and Freundlich. It appears that both chemical and physical processes are responsible for adsorption. In the spirit of promoting environmental sustainability, this work shows that simultaneous management of solid waste (hazelnut shells) can be used in water treatment processes.

Future research will focus on the removal of new contaminants at environmentally relevant (low) concentrations.

List of abbreviations
Popis kratica

DCF – diclofenac
– diklofenak

HS – hazelnut shells
– ljuske lješnjaka

MHS – modified activated carbon from hazelnut shells
– modificirani aktivni ugljen iz ljuske lješnjaka

C – activated carbon Cullar
– aktivni ugljen Cullar

MC – modified activated carbon Cullar
– modificirani aktivni ugljen Cullar

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SAŽETAK

Adsorpcija diklofenaka na aktivnim ugljenima

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Prisutnost farmaceutskih spojeva u prirodnim vodama tema je brojnih znanstvenih istraživanja tijekom prošlog stoljeća zbog njihova potencijalnog negativnog utjecaja na zdravlje ljudi i okoliš. Naime, česta i prekomjerna uporaba lijekova uzrokuje njihovu čestu pojavu u komunalnim otpadnim vodama. Nažalost, međunarodne i nacionalne regulative ne nalažu kontinuirano praćenje prisutnosti lijekova u prirodnoj i pitkoj vodi, pa stoga ni procesi pročišćavanja otpadnih voda nisu usmjereni na njihovo uklanjanje iz otpadnih voda. Diklofenak (DCF), 2-[2-(2,6-dikloroanilino)fenil]octena kiselina nesteroidni je spoj koji se upotrebljava kao analagetik, protuupalni i antipiretski lijek te se često može naći u otpadnim vodama. Zbog svojih karakteristika DCF ostaje biološki aktivan u vodenom okolišu i lako ulazi u hranidbeni lanac. Stoga je DCF nužno ukloniti iz otpadnih voda prije njihova ispuštanja u vodna tijela. Adsorpcija je učinkovita i jednostavna metoda kojom se DCF može učinkovito ukloniti iz vode. Cilj ovog istraživanja je ispitati mogućnost uklanjanja DCF-a adsorpcijom na modificirane ljuske lješnjaka, modificirani i izvorni oblik komercijalnog aktivnog ugljena Cullar (Cadriano, Italija). Svojstva adsorbensa ispitana su FTIR spektroskopijom, analizom zeta-potencijala i pH_{pzc}. Učinkovitost adsorbensa ispitana je u području pH vrijednosti od 2 do 10 te opisana izotermnim modelima. Među ispitanim adsorbensima, najveća količina DCF-a od 48,7 $mg\,g^{-1}$ adsorbirana je na modificirani aktivni ugljen Cullar, dok su dobiveni rezultati dobro opisani i Freundlichovom i Langmuirovom izotermom. Značajne količine DCF-a adsorbirane su i na modificirani aktivni ugljen iz ljuski lješnjaka.

Ključne riječi
Aktivni ugljen, diklofenak, adsorpcija, voda

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