

A Review on Diclofenac Removal from Aqueous Solution, Emphasizing on Adsorption Method

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ABSTRACT: Diclofenac is a drug with an analgesic effect that accumulates and results in adverse consequences if it enters the human body more than needed. Low concentrations of diclofenac have been detected in different water resources through leachates of landfills and agricultural areas, human and animal excreta, expired drug discharge, and hospital effluents. To eliminate diclofenac from the aquatic environment, different removal methods such as membrane filtration, ozonation, advanced oxidation, Fenton oxidation, electrochemical oxidation, photocatalysis, soil aquifer treatment, ion exchange, and adsorption are studied. Adsorption is considered to be more effective and economical than other methods in case of wastewater treatment. In this review paper, studies on diclofenac removal applying different methods, especially adsorption, are inquired and the adsorbents are divided into two main categories; carbonaceous and other adsorbents. The effect of different parameters such as contact time, pH, adsorbent dosage, initial concentration, and temperature on the adsorption process in the related studies is also mentioned. Furthermore, the equilibrium isotherms and the adsorption kinetics of the studies were also noted. By studying the literature, it was clear that the pH value was a key parameter among all, because it has a main effect on the removal efficiency and it is dependent on the pK_a of diclofenac and the pH_{ZPC} of the adsorbent.

KEYWORDS: Adsorbent; Adsorption; Diclofenac; Removal methods.

INTRODUCTION

As the human population grew during recent decades, the quality of drinking water decreased and the need for drinking-water supplies is considered to become more crucial [1-3]. The main sources of spreading pharmaceuticals to the environment include administration of pharmaceuticals in human or animal therapy or food additives in livestock breeding [4]. Pharmaceuticals can also reach the groundwater through leaching in agricultural areas, leaking of sewer lines and landfill leachates [4]. In addition, human urine and feces

that make their way through municipal or sewage wastewater are considered to be a significant source [5]. Pharmaceuticals and Personal Care Products (PPCPs) also penetrate to wastewater systems during showering and the disposal of unused or expired medications into the toilet [6]. Hospital effluents are complex mixtures of compounds, among which a great number of pharmaceuticals and their metabolites can be found [7]. Pharmaceuticals end up in surface waters because they majorly escape the WasteWater Treatment Plants (WWTPs)

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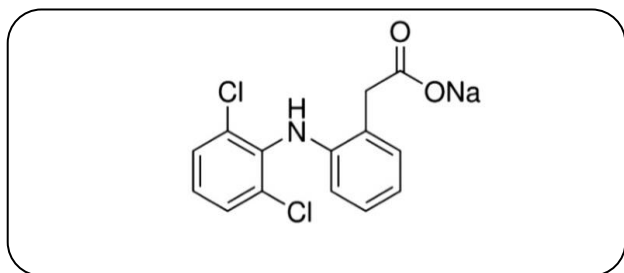


Fig. 1: Chemical structure of diclofenac sodium [5].

processes. [8]. The presence of pharmaceutical compounds in the environment is a menace to both the environment and public health due to long-term effects related to their physicochemical properties, particularly polarity, water solubility, persistence, microbial resistance and bioaccumulation in food chain [9]. Pharmaceuticals are a vast group and it has been estimated that 3000 different substances are used as pharmaceuticals [10]. The consumption of pharmaceuticals varies in different countries and even from one city to another [8]. Diclofenac (DCF), with a molecular weight of 296.148 g/mol and pKa of 4.2, which is also used as its sodium salt (DS), with a molecular weight of 318.129 g/mol, is a non-steroidal anti-inflammatory pharmaceutical and is used in human medical care as an analgesic compound [9]. Fig. 1 shows the chemical structure of diclofenac sodium.

Diclofenac is mostly used in case of inflammatory and painful diseases of rheumatism and arthritis [5]. The continual intake of even little amounts of diclofenac in human body shows several unfavorable effects such as cytotoxicity to liver, kidney and gill cells, renal lesions, platelet dysfunction, convulsion, as well as tissue damages [5, 11, 12]. Diclofenac and the hormones 17β -estradiol and 17α -ethinylestradiol are considered to be the prioritized contaminants in the aquatic environment [7, 13]. Diclofenac is widely present in water surroundings because of its low biodegradability. Accordingly, the presence of diclofenac in aquatic environment at even $\mu\text{g/L}$ concentrations is determined to cause problems due to its long exposure effects [14]. The limit of detection of DCF is reported to be 6 ng/L [15], 1 to 7 ng/L [16], and 10 ng/L [17]. Table (1) represents a summary of diclofenac concentrations reported in different aquatic environments.

REMOVAL METHODS

The elimination of diclofenac in aquatic environments

is of great importance [18]. The efficiency of diclofenac removal in sewage treatment plants reaches a maximum of 21% to 40% [12, 19]. Conventional methods for DCF removal consist of ion exchange and adsorption [20]. Other recent methods include membrane filtration, ozonation, advanced oxidation process, Fenton oxidation, electrochemical oxidation, photocatalysis and soil aquifer treatment [10, 21].

Membrane technologies are often utilized in a combination of physical, chemical and biological processes to improve the removal efficiency [10]. In 2017 *Seifollahi et al.* studied the extraction of diclofenac from aqueous solution by emulsion liquid membrane prepared by using tetrabutylammonium bromide (TBAB) as the carrier, Span 80 as a surfactant and dichloromethane as the solvent [22].

Ozonation is used for drinking water treatment and in some cases for wastewater treatment applications [18]. Ozone reacts with organic compounds in either a direct reaction as molecular ozone or an indirect reaction through the formation of secondary oxidants [18]. In 2018, *Hu and Xia* inquired modified ozonation by micro-nano-bubbles to help a rapid mass transfer and flow with groundwater [23]. In a study on the degradation of diclofenac by ozonation and advanced oxidation processes conducted by *Hama Aziz et al.* in 2017, direct ozonation in darkness proved to be very effective for the degradation of diclofenac [24].

Advanced Oxidation Processes (AOPs) are proved to be successful for the removal of a wide range of organic micro-pollutants for drinking water production [25]. AOPs enhance the elimination of pollutants by direct degradation when combined with traditional treatments [26]. *Yu et al.* in 2013 investigated the degradation of diclofenac by Advanced Oxidation and Reduction Process (AO/RP) and it was concluded that the advanced reduction process is more suitable for toxicity removal [27].

Fenton oxidation relates to the processes during which, highly reactive oxygen species are formed. *Bae et al.* studied the degradation of diclofenac by pyrite catalyzed Fenton oxidation in 2013. In comparison to the classic Fenton system which removed only 65% of diclofenac in 180 seconds, this system resulted in complete degradation within 120 seconds without formation of toxic products [28].

Table 1: Summary of diclofenac concentrations reported in different aquatic environments.

Water resource	Concentration	Reference
Urban effluents	8.8-127 ng/L	[29]
Surface water	1.1-6.8 ng/L	[29]
WWTP influents	9-13 ng/L	[30]
Liao River	717 ng/L	[31]
Surface water	25 ng/L	[4]
Selected UK estuaries	<8-195 ng/L	[32]
Drinking water in Berlin, Germany	<10 ng/L	[32]
River Rhine, Germany	0.015-0.304 µg/L	[32]
Groundwater wells, Germany	Not detected-0.38 µg/L	[32]
Selected wastewater treatment works, Germany	0.038-0.489 µg/L	[32]
Amanzimtoti WWTP influent	9.2 µg/L	[33]
Amanzimtoti WWTP effluent	8.8 µg/L	[33]
New Germany WWTP influent	21 µg/L	[33]
New Germany WWTP effluent	2.6 µg/L	[33]
Shallcross WWTP influent	53 µg/L	[33]
Mariannridge WWTP influent	6.2 µg/L	[33]
Umhlatuzana WWTP effluent	3.5 µg/L	[33]

One of the AOP methods is electrochemical oxidation. In this process, pollutants are oxidized in direct or indirect ways. One of the most important electrochemical techniques is Anodic Oxidation (AO) [34]. Studies have been conducted on the degradation of diclofenac by this method [35-37]. In 2018, *Thiruppathi et al.* investigated the photocatalytic degradation of DCF. DCF was thoroughly degraded within 80 minutes irradiation under UV light [38].

Soil aquifer treatment has good efficiency in sewage effluents for several pharmaceuticals after the secondary treatment of wastewater [39]. The advantages of this method are considered being low-cost, sustainable, and capable of targeting multi-objectives. In 2016, *Chiron and Duwig* inquired the biotic nitrosation of diclofenac in a soil aquifer system [40]. In another study in 2016, *He et al.* investigated the removal of some pharmaceuticals, including diclofenac, by soil aquifer treatment [41].

Ion exchange is a process in which ions, which are the functional groups within a solid matrix, change their place with mobile ions from a liquid phase due to electrostatic forces [42]. Although ion exchange and

adsorption are similar because in both a mass transfer from a fluid to a solid phase takes place, the delicate differences distinguishing these processes are also important [43]. Literature studies on DCF removal by ion exchange can be found in the section of "zeolites/resins" in this paper.

Adsorption is a surface phenomenon in which the molecules or ions adhere to the surface of an adsorbent. Adsorption can be physical (physisorption) or chemical (chemisorption) [44]. In physisorption no changes occur in the identity of the adsorbed molecules and the process is reversible. On the other hand, chemisorbed molecules are bonded to the adsorbent by stronger electrostatic forces, commonly undergo reaction, cannot be recovered by desorption, and the process is irreversible [6, 45]. Adsorption capacity is the maximum amount of the solute adsorbed onto the adsorbent while equilibrium conditions are set [46]. Adsorption is proved to be highly efficient and the most economical treatment method for the removal of pollutants from wastewater effluents. Also different adsorbents are rather inexpensive and available

[45, 47-49]. The necessary characteristics for an effective adsorbent are assumed to be large specific surface area, developed pore structure, good mechanical strength, and easy regeneration [14]. When choosing the suitable adsorbent, the performance, the availability, and the cost of the adsorbent are also considered [48]. In order to describe the adsorption process, different isotherm models are fitted to the experimental data and compared [50-52]. In this review paper, the focus is on the adsorption method and in the following, different adsorbents used for DCF removal and the effects of different parameters on the adsorption process are studied.

CARBONACEOUS ADSORBENTS

Carbonaceous adsorbents are carbon nanotubes, activated carbon, charcoal, activated sludge and graphite. Adsorption of an organic adsorbate from a polar solvent (water) onto a nonpolar adsorbent (carbon-based materials) is reported to be effective for a variety of micro-pollutants, particularly for uncharged and nonpolar compounds [45].

Carbon nanotubes

Carbon NanoTubes (CNTs) are mainly categorized into Single-Walled Carbon NanoTubes (SWCNTs) and Multi-Walled Carbon NanoTubes (MWCNTs) [53]. The adsorption characteristics of CNTs depend on the degree of curl, the generation of the original sheet, internal geometry, diameter, physical-chemical properties and the synthesis process. SWCNTs have more efficiency for the removal of pharmaceuticals than MWCNTs. This is probably because the exposed surface area is larger in SWCNTs and the pores are more attainable [14, 46, 53]. The ends and sidewalls of CNTs can easily be modified by attaching almost any desired chemical species [53]. Modification also increases the surface area and hence the adsorption capacity [46]. CNTs are super-hydrophobic materials that may strongly interact with aromatic pollutants through π - π coupling because they contain cylindrical graphite sheets which have very high Van der Waals index [2, 54].

Hu et al. investigated the removal of DCF from aqueous solution with MWCNTs modified by nitric acid in 2015. The purified MWCNTs represented a rapid adsorption in the first 5 minutes, the removal efficiency reached 86.5%, and the adsorption capacity was 8.01 mg/g. At pH=5, the adsorption capacity and removal

efficiency reached their maximum values. This was because at low pH values copious protons in the solution associated the adsorption of DCF to the active sites. MWCNTs with different particulate diameters all had high removal efficiency which increased gradually with the amount of MWCNTs. DCF initial concentrations in the range of 5 to 50 mg/L were brought into contact with 270 mg MWCNTs. By increasing the concentration from 5 to 12.5 mg/L, the removal percent increased from 90% to the maximum value of 95%, and after that the removal efficiency changed a little. Adsorption capacity and removal efficiency were adversely proportionate to the temperature. Freundlich isotherm model and pseudo second order kinetic equation described the process best. The adsorption process was probably controlled by both external mass transfer and intraparticle diffusion. The MWCNTs used in the study had different particulate diameters. The MWCNTs of 10-30 nm showed the highest removal efficiency (94.6%). In comparison, the MWCNTs with the particulate diameter more than 50 nm reached to a maximum of 89.7% removal efficiency [14].

In 2013, Wei et al. applied novel granular multi-walled carbon nanotubes/alumina (Al_2O_3) hybrid adsorbents to investigate the removal of DCF and carbamazepine (CBZ) from aqueous solution. In a pH range of 4 to 10, DCF removal decreased rapidly with increasing pH. The isoelectric point of the CNTs was at pH=3.2. Considering the presence of alumina in the adsorbent, the adsorption of DCF on the alumina was expected to occur easily in acidic pH values since the isoelectric pH of the γ -alumina was 8.3. But the adsorption of DCF on alumina was much less than that on the CNTs/ Al_2O_3 , so the effect of pH on DCF adsorption on alumina compared to the adsorbent was negligible. The mass ratios of CNTs/ Al_2O_3 of 1:1 to 1:9 were applied in the experiment process. The removal efficiency increased proportionally by increasing the mass ratio. The removal percent of DCF by CNTs/ Al_2O_3 (1:1) was 64.2%. The Langmuir equation adjusted to the data very well for both DCF and CBZ. The dominant mechanisms involved in DCF adsorption were the π - π electron donor-acceptor interactions and the Van der Waals forces. When MWCNTs with smaller outer diameter were used, the adsorption capacity increased. The specific surface area of CNTs/ Al_2O_3 was 237 m^2/g which was higher than that of pure CNTs (76 m^2/g), probably due to the newly exposed surface area of dispersed CNTs in the CNTs/ Al_2O_3 [55].

Activated carbon

Activated carbon is a dominant choice as adsorbent in case of the pharmaceutical removal from water because of its large surface area, abundant pore structures, and great potential in the removal of organic pollutants from aqueous solutions [46, 56]. It can be synthesized from a wide variety of natural sources and through different preparation processes [46]. Palm shell [57, 58], sawdust [59-62], walnut wood [63, 64], coconut husk [65, 66], rice husk [67], cocoa pod husk [12], olive stones [9], potato peels [68], and industrial byproducts [69] can be processed to obtain activated carbon.

In 2017, de Luna *et al.* investigated DCF removal by activated carbon derived from cocoa pod husks (CPHAC). The optimum contact time was 15 minutes and the equilibrium time was 45 minutes. The highest and the lowest DCF removal were achieved at pH values of 3 and 11, respectively. These results indicated that the percentage of DCF removal decreased with an increase in pH value, which was due to the increase in physical adsorption through Van der Waals interaction between DCF and CPHAC at low pH values. At $\text{pH} > \text{pK}_a$ and $\text{pH} > \text{pH}_{\text{ZPC}}$, DCF molecules were negatively charged, so was the surface of the adsorbent. In this case, the repulsion between the adsorbate and the adsorbent resulted in lower DCF removal. By increasing the adsorbent amount from 0.25 to 0.5 g, DCF removal increased from 89.8% to 91.4% due to the additional available active sites. By increasing DCF initial concentration from 15 to 30 mg/L, the system reached equilibrium 20 minutes sooner, and also an increase in the removal percent from 16.4% to 22.8% was reported. Freundlich model was suitable for describing the experimental data and pseudo second order model showed a good correlation for DCF adsorption on CPHAC. Also, the mechanism of adsorption was chemisorption [12].

In another study conducted by Larous in 2016, activated carbon prepared from olive stones was used for DCF adsorption from aqueous solution. The surface area of activated carbon prepared from olive stones was 83.72 m^2/g . Initial DCF solutions with concentrations of 25 to 150 mg/L were used. After 30 minutes the system reached equilibrium. Adsorption was investigated in a pH range of 2 to 10, the optimum pH evaluated to be 2, and the equilibrium pH was 4.2. Different amounts of the adsorbent from 2 to 7 g/L were used. The adsorption

efficiency increased by increasing the adsorbent dose. The adsorption capacity at equilibrium increased with an increase in the initial DCF concentration from 5 to 60 mg/L. The experimental data best fitted BET model and the adsorption followed pseudo second order kinetic model. Film diffusion and intraparticle diffusion were the dominant mechanisms of the adsorption process [9].

In 2016, Torabi-Hokmabadi *et al.* investigated DCF adsorption from aqueous solution using NH_4Cl -induced activated carbon. The effect of contact time was studied, using a variety of contact times in the range of 1-50 minutes, while the DCF concentration was set from 10 to 100 mg/L. The optimum contact time and initial concentration were 10 minutes and 50 mg/L, respectively. Increasing the contact time from 10 to 40 minutes caused the removal efficiency to increase from 62.5 to 100%. A pH range of 2 to 10 was investigated with 50 mg/L DCF, 0.8 g/L adsorbent dosage and 10 minutes contact time. By increasing the pH value from 2 to 6, the removal efficiency increased from 53.5% to 79%. The effect of adsorbent dosage on the process was assessed by varying the NH_4Cl -induced activated carbon powder amount from 0.4 to 2 g/L in 10 minutes of contact time. Increasing the adsorbent dosage was proportional to the removal efficiency, due to the increase in adsorption sites. The optimum adsorbent dosage evaluated to be 0.8 g/L. By increasing the temperature from 10 to 20 $^\circ\text{C}$, the removal efficiency enhanced from 73 to 80%. On the other hand, by continuing to increase the temperature to 40 $^\circ\text{C}$, the removal efficiency decreased to 65.7%. The enhancement in removal efficiency was related to better interactions between the adsorbate and the adsorption sites, and decreasing the removal efficiency was due to the dissipation of the adsorbed DCF and its return to the solution. Langmuir isotherm model fitted the experimental data best. Activated carbon induced by NH_4Cl had high rate and capacity in DCF adsorption due to the great surface area and the presence of functional groups. High surface area and excellent adsorption capacity were probably due to the origin of the carbonaceous adsorbent accompanied by the explosive characteristic of NH_4Cl which helped to increase the adsorbent porosity during preparation [70].

In 2016, Jodeh *et al.* prepared activated carbon from Cyclamen Persicum Tubers (CTAC) for DCF removal from aqueous solution and compared the adsorbent

with Eucarbon. The system reached equilibrium after 120 minutes for CTAC and after 150 minutes for Eucarbon. The optimum pH for DCF adsorption was 2 for each adsorbent. This indicated that at pH values lower than the pK_a of DCF, the Van der Waals interactions between DCF and the adsorbent surface increased. Different amounts of the adsorbent ranging from 0.1 to 0.8 g were used in the experiment. DCF removal percent increased by increasing the adsorbent dosage for both adsorbents due to more available active sites. Adsorption of DCF decreased with a rise in temperature because DCF had more affinity to the solvent than to the adsorbent. Besides, the physical interactions diminished by increasing the temperature. The highest adsorbed amount of DCF at 15 °C was 83.58% by CTAC and 74% by Eucarbon. Also the ΔH° was less than 40 kJ/mol, indicating a physisorption process. The thermodynamic studies on the changes in free energy showed that the adsorption of DCF on CTAC was spontaneous and temperature dependent. Freundlich isotherm fitted the experimental data and pseudo second order kinetic model described the process. The optimum DCF removal percent was 82% for 0.7 g CTAC at DCF concentration of 70 mg/L, and it was 77% for Eucarbon [71].

OTHER ADSORBENTS

Zeolites/Resins

The resins, both natural and artificial, are commonly referred to as zeolites [45]. Zeolites contain two types of cations named located cations and free cations [42]. Hydrophobic zeolites have some advantages such as thermal stability, precise pore size distributions, selective adsorption and non-flammability [72]. Surfactants are divided into nonionic, cationic, anionic, and zwitterionic/amphoteric groups [3]. Zeolites show little affinity to adsorb a negative organic ion (like DCF), so they are commonly modified by surfactants. Modification of zeolites with a long chain of organic cations leads to an increased surface, hence provides high dependency for organic pharmaceuticals [11].

The removal of DCF, atenolol and salicylic acid by modified hierarchical ZSM-5 zeolite was investigated by *Rac et al.* in 2018. Hierarchical zeolites possess mesopores besides their inherited micropores. These formed mesopores can provide accessible sites to larger guest species and extend the application of the zeolite. The ZSM-5 zeolite had a SiO_2/Al_2O_3 ratio of 50. Mesopore

formation in the adsorbent was achieved via alkaline treatment. Initial solution concentrations were in the range of 10^{-5} to 10^{-3} M. For a certain dose of the adsorbate, the adsorption process was conducted through different contact times of 15 to 360 minutes. Experimental data of DCF adsorption fitted the Toth isotherm equation and the thermodynamic investigation showed that the heat of adsorption was about 45 kJ/mol. The modification of ZSM-5 zeolite pore structure through alkaline treatment showed an increase in the total pore volume (from 0.236 to 0.449 cm^3/g), mesopore volume (from 0.085 to 0.380 cm^3/g), BET surface (from 365 to 470 m^2/g), and external surface (from 65 to 173 m^2/g) related to the mesopore formation, while only a slight decrease in micropore volume was measured (from 0.144 to 0.138 cm^3/g). The total SiO_2/Al_2O_3 ratio decreased from 50 to 43 after the alkaline treatment, but it reached 50 again after the subsequent acid wash. The maximum adsorbed amount of DCF increased moderately after the alkaline treatment. This was because the appeared mesopores in the adsorbent structure presented more active sites for the adsorbate to interact with. The molecules in the hierarchical zeolite were able to bind to the adsorption sites which were inaccessible before modification [73].

Sun et al. investigated the adsorption and retention of DCF on modified zeolite in 2017. Cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) were used for zeolite modification. The zeolite external cation exchange capacity (ECEC) was enhanced to 200% by modification. The adsorption of DCF on the adsorbent was fast, and in 2 hours the system reached equilibrium. The fast adsorption process indicated that the adsorption sites were on the external surface of the adsorbent. The equilibrium pH was increased from 2.2 to 5.7 and this caused a slight increase in DCF adsorption from 77 to 79 mmol/kg. By increasing the temperature from 295 to 325 K, the ΔG value increased slightly from -17 to -15 kJ/mol. According to this, the reaction was slightly exothermic. In comparison, the adsorption of DCF on activated carbon from *Cyclamen Persicum* Tubers (a previously mentioned study) showed a small increase in ΔG value from -3.0 to -1.6 kJ/mol as temperature increased from 288 to 318 K. Langmuir adsorption isotherm found to be the most appropriate isotherm and pseudo second order kinetic equation best fitted the experimental data. The loading level of CTAB also

affected the zeta potential and the zeta potential became progressively positive by increasing the level of CTAB loaded on the zeolite. According to this, the positively charged zeolite effectively interacted with negative DCF at pH values greater than the pK_a . The surfactant modification of the zeolite caused the anion exchange with DCF accompany the partitioning of DCF into the adsorbed surfactant micelles, hence improving DCF adsorption [74].

Lu *et al.* investigated the adsorption of DCF and clofibrac acid (CA) on MIEX resin in a single and bi-component batch system in 2016. At first, the adsorption was fast because of the abundant adsorption sites, then it continued slowly to reach equilibrium. While the MIEX resin demonstrated a strong pH tolerance, the uptakes of DCF on the adsorbent were higher for a pH range of 5 to 9. For lower pH values (pH=3) or higher pH values (pH=11), a fall in the tendency of the adsorption was observed due to less interaction between the adsorbate and the resin. MIEX resin doses ranging from 0.2 to 1.4 mg/L were applied in the experiment. From 0.2 to 1.0 mg/L of the adsorbent dosage, the removal efficiency of DCF increased from 75.81% to 96.14%, and the optimum adsorbent dosage evaluated to be 1.0 mg/L. The results were also in agreement with the results of another [75] study. Freundlich isotherm model and pseudo first order kinetic model described DCF adsorption on MIEX resin. Thermodynamic analysis showed that the adsorption of DCF was endothermic. The investigation of Gibbs free energy values confirmed a spontaneous adsorption process for DCF. The external mass transfer and surface diffusion controlled the adsorption process simultaneously. The maximum adsorption capacity of the MIEX resin was 322.31 mg/g [76].

In a complementary study, the adsorption and release of DCF by modified natural zeolite composites conducted by Krajišnik *et al.* in 2013 were investigated. The results of cationic surfactant hexadecyltrimethylammonium bromide (HB) modified natural zeolite composites at three different levels (10, 20 and 30 mmol/100 g) in a buffer solution were compared to data from another study [77]. The raw material used for the preparation of the composite was clinoptilolite-rich tuff. The electrokinetic mobility of the adsorbent changed during the process. The electrokinetic mobility of the complex after DCF adsorption onto the adsorbent was assessed

to verify the changes. According to the measured values, the presence of DCF molecules on the surface of the adsorbent was obvious. The maximum adsorbed amount of DCF was 74 mmol/kg for ZHB-10 and 142 mmol/kg for ZHB-20 [11].

In another study by Krajišnik *et al.* in 2011, the adsorption of DCF on clinoptilolite zeolite modified with cetylpyridinium chloride (CPC) was investigated. DCF solutions with a concentration range from 0.16 to 1.57 mmol/L in a phosphate buffer at pH=7.4 were prepared. An amount of 200 mg of each zeolite composite was added to 50 mL solutions. The Langmuir isotherm was the best isotherm model describing the experimental data. The effect of loaded surfactant on the zeta potential of the zeolite was also verified. The initial zeta potential of the starting zeolite was -27.4 mV. When the concentration of the loaded surfactant was equal to 100% of ECEC, the zeta potential of the composite became -8.4 mV. By increasing the surfactant loading to 200% of ECEC, zeta potential changed drastically to +29.7 mV. After the modification of zeolite with surfactant equal to 300% of ECEC, zeta potential was measured to be +32.2 mV. Also, when the surfactant amount was equal to 100% of ECEC, the modified zeolite surface tended to be more hydrophobic. This effect advanced the adsorption of DCF onto the adsorbent. In general, when the amount of the loaded surfactant was above the ECEC value of the zeolite, less extended bilayers and admicelles existed on the adsorbent surface, so the anionic DCF was adsorbed by anion exchange as well as partitioning mechanism. Also the interactions between the hydrophobic parts of the surfactant and DCF helped the adsorption process. As a result, the uptake of the adsorbate increased after modification with the surfactant. As the CPC amounts increased, the organic molecules were both chemically and physically adsorbed to the zeolite surface [78].

Grape bagasse

A novel adsorbent derived from a natural origin was introduced by Antunes *et al.* in 2012. The study was aimed to evaluate the characteristics of Isabel grape bagasse and assess its efficiency in DCF removal from aqueous solution. The process was faster in the beginning of the experiment. The maximum adsorption capacity was after several hours of contact time. The optimum pH was lower than 3.59, because

the surface of the adsorbent was positively charged. On the other hand, at pH values less than pK_a of DCF, DCF was present in its neutral form and its solubility in water decreased. After all, the initial pH of DCF solutions was chosen to be in its natural pH in Milli-Q water, which was about 5.0, and did not go through any further adjustments. DCF initial concentration was in the range of 5-30 mg/L. Freundlich model fitted the experimental data. The adsorption process was in good agreement with pseudo second order equation. The external diffusion model did not fit with the experimental data very well. On the other hand, with the intraparticle diffusion mechanism, the adsorption presented linear portions which meant the adsorption could be defined with this mechanism. The BET surface area detected to be low (about 2 m²/g). This surface area was smaller than that of carbon black and activated carbon, but was superior to other biomass materials such as rice husk and rice bran. Also, desorption of DCF through continuous agitation of the system after equilibrium validated that the process of DCF adsorption by grape bagasse was completely reversible which resulted in the excess lifetime of the adsorbent [19].

Chitosan

Chitosan is a biopolymer obtained by deacetylation of chitin, which is abundantly available in nature. Chitosan is an environmentally friendly, easily digested, nontoxic, quite cheap and abundant substance. In a study on the removal of DCF with chitosan modified with acetylacetone and ethylenediamine by *Pereira et al.* in 2014, the shorter adsorption time compared to when other adsorbents were applied, was the key feature of this adsorbent. A DCF initial concentration of 30 mg/L with 35 mg of the adsorbent and contact times ranging from 0 to 150 minutes were studied. The maximum adsorbed amount of DCF was reported within 45 minutes and after that, only a little variation occurred. According to this, the adsorption process occurred at excellent contact time compared to a previously mentioned study by *Antunes et al.* which led to the equilibrium contact time of 80 minutes for the same concentration. HCl or NaOH solutions were used to adjust pH in a range of 3 to 10. The highest DCF adsorbed amount was at pH=4, and it decreased by increasing the pH value. The results were in agreement with the previously mentioned study by *Antunes et al.*

in which the optimum pH value was 5.0. Pseudo second order kinetic model described the experimental data. Modification of chitosan with acetylacetone and ethylenediamine enriched its nitrogen (to 5.66 mmol/g) and carbon (to 35.00 mmol/g) content, causing an increase in C/N ratio from 6.13 to 6.18 compared to the pure chitosan [79].

Graphene oxide

Nam et al. studied the adsorption of DCF and sulfamethoxazole (SMX) on graphene oxide in aqueous solution in 2015. Both DCF and SMX systems reached equilibrium within 24 hours, and at this point DCF removal was 50%. A pH range of 3 to 11 was examined and pH adjustment was done with NaOH or HCl solutions. Under acidic conditions, the π - π interaction force led to a more effective adsorption. Freundlich isotherm model fitted well to the experimental data before and after the adsorbent modification. The main interaction mechanisms between the species and the adsorbent were hydrophobic and π - π electron donor-acceptor interactions. Also, DCF tended to interact with the graphitic structure of the adsorbent more than SMX, because of its greater exposed surface area to the adsorbent. The maximum removal was 50%. In order to improve this amount, graphene oxide solution was modified by sonication. This modification caused the maximum removal for DCF reach 75% [80].

Clay minerals and soils

Clays are aluminosilicate minerals, mostly colloidal remains of sediments and rocks. They are rather applicable adsorbents for the removal of pharmaceuticals because of their ability to exchange ions with acidic or basic compounds [46].

Sun et al. investigated the removal of DCF from water using surfactant modified clay minerals in 2017. Different amounts of cationic surfactant cetyltrimethylammonium bromide (CTAB) were applied to prepare 2:1 clay minerals illite and montmorillonite (MMT). 0.07 g of the adsorbent was added to 20 mL of DCF solutions in a concentration range of 0.5 to 5.0 mmol/L for 24 hours. A CTAB bilayer formation enhanced DCF adsorption significantly due to the formation of admicelles. Increasing the amount of loaded surfactant on the adsorbent also enhanced Van der Waals interactions

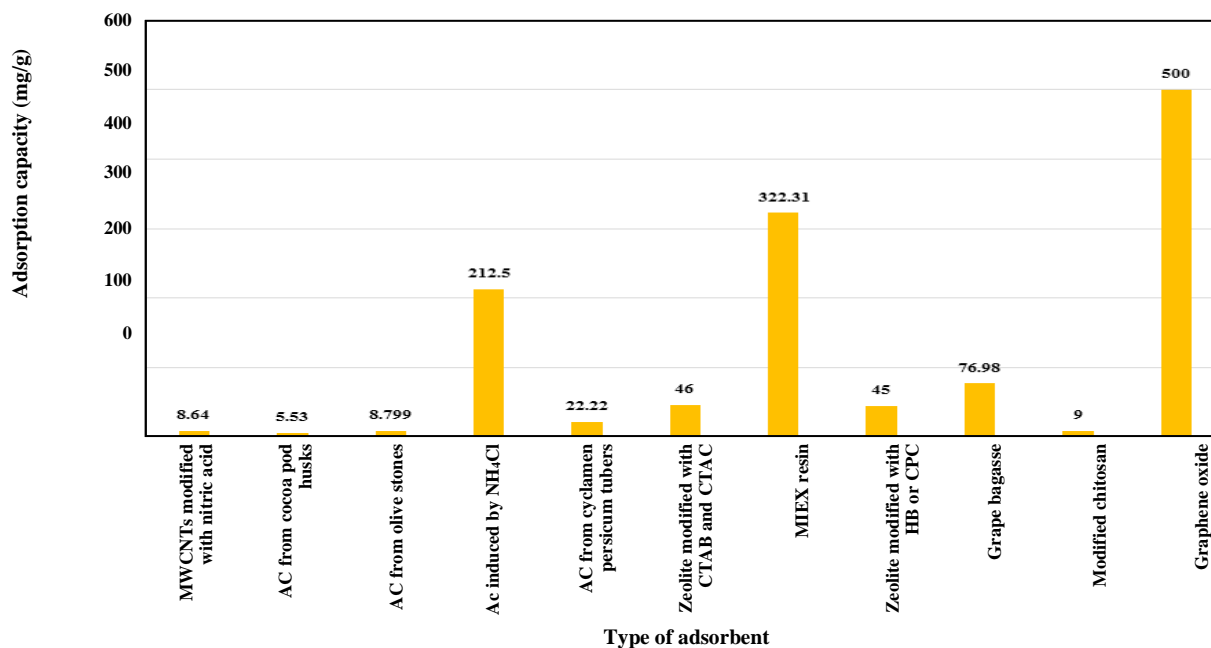


Fig. 2: Adsorption capacity of different adsorbents.

between the adsorbent and DCF by increasing the adsorbent hydrophobic characteristic [81].

In 2017, *De Oliveira et al.* investigated the adsorption of DCF onto organoclays modified with benzyldimethyltetradecylammonium (BDTA) and hexadecyltrimethylammonium bromide (HDTMA) cationic surfactants. BDTA surfactant had better effects than HDTMA. This difference was related to the π - π interactions between BDTA and DCF which led to an enhanced adsorption. The nature of the surfactant also changed the specific surface area of the clay mineral and influenced the uptake of DCF. Clay minerals used for DCF removal were geosorbents which resulted in stable complexes at the end of the process [50].

Grauer-Bacart et al. investigated the adsorption and co-adsorption of DCF and Cu (II) on calcareous soils in 2016. DCF solutions were added to 1 g of soil to reach concentrations ranging from 1 to 100 $\mu\text{mol/L}$. The organic matter and CaCO_3 could have possible opposite effects on DCF adsorption. A decrease in organic matter or an increase in CaCO_3 content resulted in a significantly increased mobility of DCF in the soils, which confirmed the adverse effect of CaCO_3 . An enhancement in DCF adsorption in the presence of copper was anticipated due to the competitive effect and complex formation, but the presence of Cu (II) had no considerable effects on DCF adsorption. This was probably due to the formation of

copper hydroxides form the existing Cu (II) in basic conditions of the calcareous soils, instead of associating the formation of Cu (II)-DCF complex [82].

Xu et al. investigated the degradation and adsorption of DCF and five other PPCPs in agricultural soils in 2009. 5 grams of each soil was brought into contact with 10 mL of 0.01 M CaCl_2 solution containing concentrations of 0 to 10 mg/L of the targeted PPCPs. The degradation of PPCPs was influenced by the organic matter and clay contents of the soil. Results also showed that the degradation of DCF and the other five components was faster in nonsterile soil than in sterilized soil [83].

Choosing the suitable adsorbent is one of the major steps in an adsorption process. Among the necessary characteristics for an adsorbent mentioned earlier in this study, the adsorption capacity is very important. Fig. 2 shows the adsorption capacity of some of the adsorbents mentioned before based on the literature studies by different authors. It can be seen from Fig. 2 that activated carbon (AC) prepared from natural sources had less capacity in DCF adsorption than modified zeolites. Also some less common adsorbents for DCF removal showed significant adsorption capacities. For selecting the appropriate adsorbent, one should consider these values as well as the process conditions, the possibility of the adsorbent preparation, the cost of the procedure, and the probability of the adsorbent regeneration.

CONCLUSIONS

One of the reoccurring contaminants in the aquatic environments is diclofenac residues. Different removal methods were used to attenuate this pharmaceutical in the aquatic environments. Adsorption is a rather effective and low-cost method and diverse adsorbents were applied to study the adsorption of diclofenac from aqueous solutions in the literature.

- The modification of the adsorbent enhances its adsorptive characteristic by changing the surface charge, providing more available surface area, or adding mesopores to the adsorbent.

- The contact time, pH, the adsorbent dosage, and the initial concentration are the key parameters affecting an adsorption process.

- Temperature also has a slight reverse effect on the adsorption of diclofenac in an aqueous solution, but this effect can be negligible since most studies were carried out in the ambient temperature.

- According to the applied adsorbent, the system reaches equilibrium within minutes or hours.

- The optimum pH is dependent on the pK_a of diclofenac and the pH_{ZPC} of the adsorbent, because these two pH values dictate the charge of diclofenac and the adsorbent and hence the interactions between them.

- The optimum adsorbent dosage is in most cases for greater amounts of the adsorbent which provide more attainable active sites.

- The initial concentration of the diclofenac solution in the experiments is normally in the range of mg/L.

- The efficiency of an adsorption process depends on the appropriate choice of the adsorbent, the modification procedure, and the optimum conditions.

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