

HOW ORGANIC MATTER CAN AFFECT IMMOBILIZATION OF DICLOFENAC IN SOILS

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<https://doi.org/10.37904/nanocon.2022.4592>

Abstract

Natural organic matter is a complex pool of organic substances which can affect the transport of both beneficial and harmful species in soil systems. The occurrence of pharmaceuticals as soil pollutants has become one of the new environmental threats. The mobility of drug contaminants in soils and their availability for plants is largely controlled by their sorption. Soils have a "self-cleaning" ability which depends on the content of organic matter. Interactions between drugs and soil organic matters can lead to the partial immobilization of these pollutants and suppression of their mobility in soil resulting in the pollution of drinking water resources, crop and consequently food contamination. In this contribution, the soils with different contents of organic matter were selected to assess their sorption abilities to widely used pharmaceutical diclofenac (non-steroidal anti-inflammatory drug that is frequently prescribed to reduce inflammation and pain). Stability of formed complexes and drug leachability in water were also studied to determine the immobilization degree of pharmaceutical in studied soils. The effect of organic matter on binding ability of soils as well as the leachability of diclofenac at different pH values are compared and discussed.

Keywords: Organic matter, diclofenac, adsorption, immobilization

1. INTRODUCTION

Diclofenac is widely used as nonsteroidal anti-inflammatory drug leaving residues in the environment. It has a low removal efficiency ranging from 5 to 81% in conventional sewage treatment and has been found in wastewater treatment plant effluents in many countries worldwide [1-4]. It is considered as a contaminant of emerging concern and has been included in the list of priority hazardous compounds [2,5] and Watch List of EU Decision 2015/495 [6-9]. Diclofenac seems to have the highest level of acute toxicity among other non-steroidal anti-inflammatory drugs tested [1,10]. Diclofenac is relatively persistent in soils under anaerobic conditions with a negligible degradation [11,12] while better degradation was observed under oxic conditions [12,13]. Recent works indicated that degradation was the main attenuation process of diclofenac during the wetting and drying cycles in soil, while adsorption was the only process controlling the fate of diclofenac under continuous infiltration conditions [12,14]. It means that adsorption would dominate the environmental fate of diclofenac in water saturated soils. Understanding the adsorption mechanism in the soil is significant for determining its ecotoxicity, migration, and conversion. Many studies have focused on the removal of diclofenac from waters by different low-cost and effective adsorbent materials [15-17]. Our contribution is focused on the adsorption of diclofenac directly by soil. The investigation of adsorption from aqueous solution onto soils is crucial for prediction of its possible immobilization, mobility and removing diclofenac contamination. In general, the interactions of pollutants in soils are affected by their physicochemical properties as well as soil properties (its structure and composition, content, and form of organic matter etc.). Other factors influencing interactions are, pH, ionic strength, temperature, contact time, presence of additional constituents, and (also) living organisms in soil systems [15-19].

Some studies dealing with the behaviour of diclofenac in soil were recently realized. Filep et al. [20] described the effect of chemical properties of pharmaceuticals on sorption behaviour in soils and goethite. They stated that the main controlling factor for ionic compounds, such as diclofenac sodium, is their charge (and Coulomb forces). Drillia et al. [21] studied the adsorption of six drugs in two soil types. Their results showed that the adsorption on the soil of the low organic carbon was not dependent only on the organic content of the matrix but also on the other matrix properties and the dissociation degree of the compounds. Diclofenac had relatively high distribution coefficients obtained for both adsorption and desorption. It means that it is not strongly bonded and can be easily leached. Kohay et al. [22] studied efficiency of polycation-clay sorbents for diclofenac. They stated that the filtration of micro- and nano-concentrations of diclofenac by composite columns, in the presence of humic acids was more efficient than by granulated activated carbon. columns. In contrast, Yu and Bi [12] stated that the adsorption of diclofenac on soil is controlled by bonding with surface -OH groups of iron oxides. Their results indicated that adsorption coefficients of diclofenac onto soils can be well predicted by contents of extractable iron instead of total iron oxides contents. The influence of iron oxides in the adsorption of diclofenac should be important mainly in soils with relatively low content of organic matter. Zhang et al. [23] studied the sorption-desorption behaviour of several pharmaceuticals including diclofenac. Their experiments were realised with individual drugs as well as a mixture of them. The proportion of diclofenac adsorbed to the soil in the mixture system was 72 % and differed slightly from the individual adsorption. Diclofenac displayed strong sorption and low desorption in both the individual-compound and mixture-compound systems. De Mastro et al. [24] compared the adsorption of sulfamethoxazole and diclofenac on three agricultural soils with different mineralogical composition and organic matter content. Their results showed that diclofenac was adsorbed moderately while sulfamethoxazole negligibly, regardless the soils. While clay minerals had little influence on their adsorption, the organic matter supported interactions of soil with diclofenac. Similarly, Graouer-Bacart et al. [25] confirmed that the mobility of diclofenac in soils increases significantly with low organic matter content (and with high CaCO₃ content), which can lead to an enhanced risk for groundwater contamination.

As can be seen, the results and conclusions presented in studies can be different. The organic matter content as well as the presence of minerals can have different effect of the interactions of diclofenac with soils and its mobility in them. In general, the mobility of the pharmaceuticals in soils, and consequently their potential for contaminating groundwaters, is shown to depend on the amount of drug applied, the intensity of the “rain” events and the soil type and composition [21].

2. MATERIALS AND METHODS

Diclofenac (CAS 15307-79-6) was purchased from Sigma-Aldrich. Soil I (phaeozem) was sampled in the region Jablůnka, soil II (alluvial soil) in the region Černotín (both closed to river Bečva). Both samples are arable soils with periodically changed arable crops as wheat and corn. Main characteristics of soil samples are listed in **Table 1**.

Table 1 Characterization of soil samples

Sample	Total organic carbon (wt.%)	Humic /fulvic acids (-)	Cation exchange capacity (mmol/g)	Humification degree (%)	Humus content (wt. %)
Soil I	2.23	1.22	0.13	12.6	3.84
Soil II	1.73	0.88	0.21	12.1	2.98

Soil samples were mixed with the solution of diclofenac (0 – 2.5 mg/dm³), stirred (48 h) and centrifuged (Hettich ROTINA 46 R; 5000 rpm, 10 minutes). The ratio between the solid powder sample and solution was 0.5 g : 25 cm³. Supernatants were filtered (0.22 μm) to remove solid particles and analysed by means of UV/VIS spectrometry (HITACHI U-3900H) to determine the residual amount of diclofenac in solution after adsorption. Simultaneously pH values and conductivities of solutions were measured.

The stability of formed complexes was investigated by means of desorption experiments. Diclofenac-soil complexes were mixed with 10 cm³ of deionized water, stirred, centrifuged, filtered, and analysed by the same methods as in the case of adsorption experiments.

To investigate the effect of pH on the adsorption, Britton–Robinson buffer solutions (at pH values equal to 5, 7, and 10) were used for the adsorption/desorption experiments. The experiments were realized only with the highest diclofenac concentration.

All experiments were realized at 25 °C (±1 °C). They were triplicated and average values are presented.

3. RESULTS AND DISCUSSION

In **Figure 1**, adsorption isotherms obtained for diclofenac adsorbed on two different soil samples are shown. It can be seen, that adsorbed amounts are much higher for soil I, which is richer in the total organic carbon (related to soil organic matter), humic acids and humus content (see **Table 1**). In contrast, the cation exchange capacity is higher for soil II. The efficiency of adsorption decreased with increasing initial concentration of diclofenac for both used soil samples. Their values ranged between 74 and 87 % for soil I; 24 and 36 % for soil II. Measured values of pH and conductivity were lower for soil II and similar as in the case of background experiments with soil and distilled water. Their dependence on the concentration of diclofenac was not significant. The pH values ranged between 7 and 7.8, conductivity between 0.2 and 0.5 mS cm⁻¹.

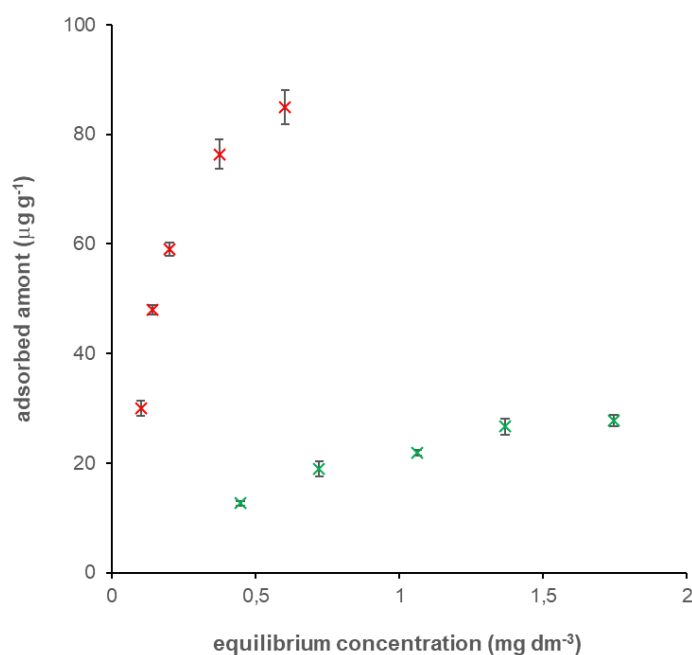


Figure 1 Adsorption isotherms obtained for soil I (red) and soil II (green).

Experimental data were fitted by Langmuir isotherm [26,27] frequently used for chemical adsorption

$$a = a_{max} \frac{bc}{1+bc}, \quad (1)$$

where a is adsorbed amount, a_{max} is adsorption capacity, c is equilibrium concentration and b is the ratio between adsorption and desorption rate constants ($b = k_{ads}/k_{des}$). Parameters of adsorption isotherm (a_{max} and b) can be determined on the basis of the linearized form of equation 1:

$$\frac{1}{a} = \frac{1}{a_{max}b} \frac{1}{c} + \frac{1}{a_{max}}. \quad (2)$$

The values of adsorption capacity a_{max} were determined as $117.6 \mu\text{g g}^{-1}$ for soil I and $48.6 \mu\text{g g}^{-1}$ for soil II. The ratio b was equal to 4.72 for soil I and 0.82 for soil II. The results indicated that soil I has not only much higher adsorption capacity but also that the adsorption is stronger in comparison with desorption one and the mobile fraction should predominate in complex of diclofenac with soil II.

Desorption experiments showed that the content of mobile fraction is relatively low for both used soil samples. A measurable desorption was indicated only for the highest amount of diclofenac adsorbed on soil I and two highest amounts of diclofenac adsorbed on soil II. However, it was confirmed that diclofenac can be desorbed more from its complex with soil II. The difference between both soil samples is less significant than can be deduced from the coefficient b in Langmuir isotherm (equation 2), which is much higher for soil I. The reason of this discrepancy can be explained by the character of Langmuir isotherm. The isotherm is based on the adsorption and desorption kinetics valid for the simplest reaction mechanism, where substance S is adsorbed on the adsorbent A (its active site) forming complex SA and can be desorbed in reverse reaction: $S + A \leftrightarrow SA$. In equilibrium, the rates of adsorption and desorption are equal and the adsorption amount as well as the concentration in solution do not change with time. Since soil is very complex system containing many different constituents, it is impossible to expect that all active sites in soil are equivalent. In contrast, soil can contain many different active sites with different bond strengths. Therefore, the above-mentioned mechanism of simple surface reaction can be considered as an idealized situation for the adsorbent which only one type of active sites (mutually independent). It means that adsorption parameters based on equation 1 and 2 can be considered as effective values including all types of active sites in given soil sample and all proceeding surface reactions.

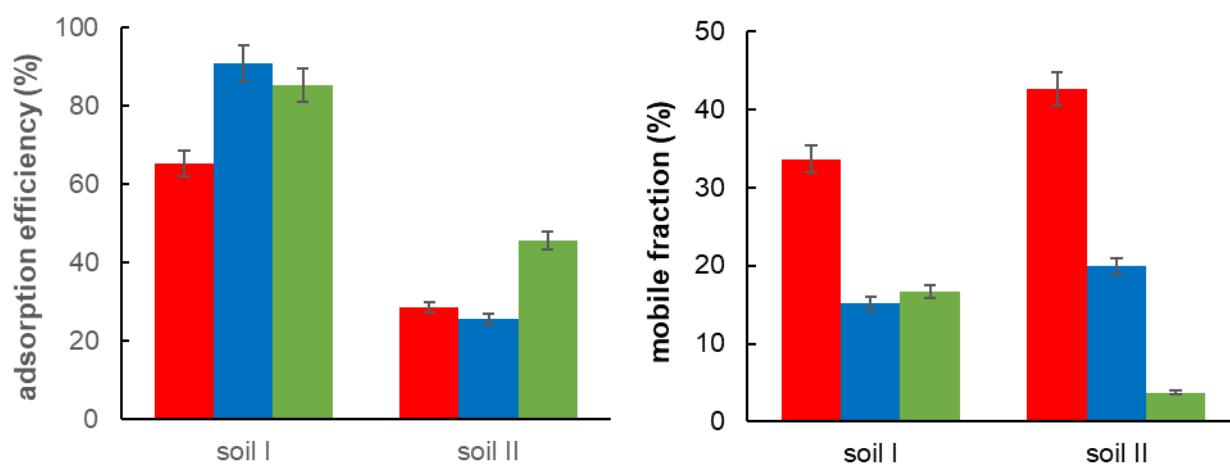


Figure 2 Adsorption efficiency and content of mobile diclofenac fraction in soils at pH 5 (red), 7 (blue) and 10 (green)

In **Figure 2**, The efficiencies of adsorption and desorption are compared. The adsorption efficiency was calculated as % adsorbed from the total amount of diclofenac in solution mixed with soil. The desorption efficiency as the amount leached from diclofenac-soil complex into water. The desorption efficiency thus can be considered as the mobile fraction of diclofenac which is leachable by water. As can be seen, the increase in pH resulted in the increase in adsorption efficiency and (also) in the increase in the bond strength. Our results are not with agreement with hypothesis of Filep et al. [20] that ionic compounds as diclofenac are bound to soil mainly by means of their charge and the importance of organic matter is negligible. In contrast, soil I richer in organic carbon was able to adsorb much higher amount of drug than soil II. It indicated that the organic matter can play important role in the immobilization of diclofenac in soil which agrees with conclusions of other authors [22-25]. Our results also confirmed the significance of the properties of organic matter and soil matrix.

4. CONCLUSION

Adsorption and desorption experiments were carried out with two soil samples of different quality. Diclofenac as widely used anti-inflammatory pharmaceutical was chosen for this study. It was confirmed that soil organic matter plays key role in the mobility and bio-availability of pharmaceuticals in soils.

It was found that the immobilization ability of soils was strongly influenced by the content of organic matter. The stability of formed complexes determined by desorption experiments showed that formed complexes are relatively stable and the stability increases with the organic carbon content. The increase in pH of used solutions resulted in more effective adsorption and the suppression of drug leachability.

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