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Removal of diclofenac potassium from wastewater using clay-micelle complex

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The presence of an ionized carboxyl group in the widely used non-steroidal anti-inflammatory (NSAID) drug diclofenac potassium results in a high mobility of diclofenac and in its low sorption under conditions of slow sand filtration or subsoil passage. No diclofenac degradation was detected in pure water or sludge during one month. Tertiary treatments of wastewater indicated that the effective removal of diclofenac was by reverse osmosis, but the removal by activated carbon was less satisfactory. This study presents an efficient method for the removal of diclofenac from water by micelle–clay composites that are positively charged, have a large surface area and include large hydrophobic domains. Adsorption of diclofenac in dispersion by charcoal and a composite micelle (otadecyltrimethylammonium [ODTMA] and clay [montmorillonite]) was investigated. Analysis by the Langmuir isotherm revealed that charcoal had a somewhat larger number of adsorption sites than the composite, but the latter had a significantly larger binding affinity for diclofenac. Filtration experiments on a solution containing 300 ppm diclofenac demonstrated poor removal by activated carbon, in contrast to very efficient removal by micelle–clay filters. In the latter case the weight of removed diclofenac exceeded half that of ODTMA in the filter. Filtration of diclofenac solutions at concentrations of 8 and 80 ppb yielded almost complete removal at flow rates of 30 and 60 mL min^{-1}. One kilogram of ODTMA in the micelle–clay filter has been estimated to remove more than 99% of diclofenac from a solution of 100 ppb during passage of more than 100 m^3.

Keywords: diclofenac potassium; micelle–clay complex; wastewater treatment; removal of anti-inflammatory drugs; kinetic studies of NSAID agents

1. Introduction

Since Ternes and Daughton [1,2] found the presence of pharmaceuticals and personal care products (PPCP) in wastewater, a significant number of studies have been conducted to determine the concentrations of a variety of pharmaceuticals and PPCPs in river waters and wastewater plants. These molecules are of wide concern because they are used frequently and are released to the environment in large quantities. Their physical and chemical properties further enhance their widespread distribution in the environment. Low concentrations of these compounds have been associated with endocrine disruption, bacteria resistance and chronic toxicity [3].

Pharmaceuticals are generally excreted after being partially or completely converted to metabolites with enhanced solubility in water, but a significant quantity of the parent drug may also be excreted unchanged. Recent studies have demonstrated that elimination of high to medium polar pharmaceuticals in municipal sewage treatment plants is often incomplete, ranging between 60% and 90%. For example, the study performed by Kolpin and co-workers has chronicled the detection of over 95 organic chemicals in US streams and rivers [4]; 7 to 38 compounds were found in water samples, together with their metabolites. Measured concentrations reported in this study were generally in the ng L^{-1} range. These results demonstrate the importance of obtaining data on metabolites as well as parent compounds, in order to fully understand the fate and transport of individual pharmaceuticals in the wastewater cycle [5].

Among the most commonly used pharmaceuticals are the non-steroidal anti-inflammatory drugs (NSAID), taken to reduce inflammation and as analgesics to reduce pain in conditions such as arthritis or acute injury. This class of compounds includes acetylsalicylic acid (e.g. 836 tons in Germany in 2001), paracetamol (e.g. 622 tons in Germany in 2001), ibuprofen (e.g. 345 tons in Germany in 2001), naproxen (e.g. 35 tons in England in 2000) and diclofenac (e.g. 86 tons in Germany in 2001), which were found to be

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ubiquitous in stream and river waters in the concentration range of a few nanograms per litre [6].

Compared with the amount of data dealing with the distribution of pharmaceutical residues in the environment, very little information is available about the fate of these residues, especially when focused on microbial activity. This is somewhat anomalous since it should be expected that microbial transformations play a dominant role during removal of polar, acidic pharmaceuticals such as diclofenac (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid) in wastewater treatment plants [6]. Inconsistent results were reported for diclofenac. Median concentrations of diclofenac in German streams (Elbe, Rhine and Main) rarely exceeded values of $50\,ng\,L^{-1}$, and were restricted to small rivers that acted as receiving waters for communal wastewater plants. The presence of an ionizable carboxyl group results in a much higher mobility of diclofenac than is indicated by its log *P* (octanol–water distribution coefficient), and in low sorption properties under the conditions of slow sand filtration or subsoil passage. Thus, it is essential to establish an efficient method for the removal of diclofenac from wastewater that should represent the most dominant sink for this drug [7].

Although water purification techniques such as granular activated carbon could potentially remove this pollutant from wastewater streams, the high cost involved suggests that more attention should be given to the optimization of current treatment processes and reduction at source in order to reduce environmental contamination [8–10]. Generally the methods used for wastewater treatment are:

1. Biodegradation: biological degradation (aerobic/anaerobic by microorganisms).
2. Deconjugation: conjugates of organic compounds such as steroid hormones have been shown to be readily deconjugated in domestic wastewater and within sewage treatment plants. It seems probable that gluconoride and sulphate conjugates of drug compounds may be degraded by the same process. The effect will be to increase the excreted contribution of the active drugs to sewage and effluents.
3. Partitioning: partitioning between the aqueous and organic biomass phases is a key component in determining the ultimate concentrations of organic pollutants. Compounds with high log *P* (lipophilic molecules) values are known to be easily sorbed from sludge, whereas substances with lower values more likely remain in the aquatic phase, depending on the individual compound; moreover, sorbed substances may also be remobilized if they are not strongly bound.
4. Removal during sludge treatment: drugs may also be degraded during sewage treatment processes. Many pharmaceuticals are not thermally stable and so might be expected to break down during processes such as composting, as a result of the heat (as well as chemical degradation and biodegradation).
5. Photodegradation: several pharmaceutical compounds have been shown to degrade through the action of sunlight. The most extensively studied of these compounds is the analgesic/anti-inflammatory drug diclofenac, which has been shown to degrade in the aquatic environment by the action of ultraviolet (UV) light [8].

In this paper we report a relatively novel method for the removal of diclofenac potassium by filters that include micelle–clay complexes. The micelle–clay composites that we used are positively charged, have a large surface area and include large hydrophobic domains. It was shown by X-ray diffraction, electron microscopy and adsorption experiments that the characteristics of the micelle–clay complexes are different from those of organo–clay complexes which are formed by adsorption of the same organic ODTMA (octadecyltrimethylammonium) cation as monomers [11]. We also employed a BDMHDA (benzyldimethylhexadecylammonium)–clay complex for testing its performance in removing diclofenac from wastewater. These micelle–clay composites have already been proven useful in the removal of about 20 neutral and anionic pollutants [12–14].

2. Experimental

2.1. Materials

All chemicals were of analytical grade. The clay used was Wyoming Na-montmorillonite SWY-2 obtained from the Source Clays Registry (Clay Mineral Society, USA). Quartz sand (grain size 0.8–1.2 mm) was obtained From Negev Industrial Minerals (Israel). ODTMA bromide was obtained from Sigma Aldrich. BDMHDA chloride was purchased from Fluka Chemie (Switzerland). Diclofenac potassium was obtained as a gift from Beit Jalah Pharmaceutical Company (Palestine). Activated charcoal (12–20 mesh) was obtained from Sigma (USA). Deionized water was used to prepare all solutions. Methanol and water for analysis were both HPLC grade and purchased from Sigma Aldrich. Magnesium sulphate was purchased from Sigma Aldrich. High purity diethyl ether (>99%) was purchased from Biolab (Israel); orthophosphoric acid was obtained from Riedel-de Haën (Germany).

The concentration of diclofenac in the $mg\,L^{-1}$ range was determined by using a Perkin Elmer Lamda 5 UV-Visible spectrophotometer. Samples were shaken using Big Bill (Banstaed/Themolyne, USA). The samples were centrifuged in a Labofuge 200 (Heraeus Sepatech, Kendero Laboratory Products, Germany).

A Shimadzu prominence high performance liquid chromatography (HPLC) system (Shimadzu Corp., Japan) was used for HPLC–MS/MS measurements.

The HPLC system consisted of a model 2695 HPLC from Waters (USA) equipped with a Waters 2996 photodiode array. Data acquisition and control were carried out using Empower™ software (Waters, USA). Analytes were separated on a 4.6 mm × 150 mm C18 XBridge® column (5 μm particle size) used in conjunction with a 4.6 mm, 20 μm, XBridge® C18 guard column. Microfilters of 0.45 μm porosity were normally used (Acrodisc® GHP, Waters). A pH meter, model HM-30G (TOA Electronics USA), was used in this study to measure the pH value of each sample.

The wastewater treatment plant (WWTP) at Al-Quds University collects a mixture of black, grey and storm water. The treatment plant consists of a primary treatment (two stage primary settling basin) and a secondary treatment (activated sludge with a hydraulic retention time of 16–20 hours, coagulation and chlorination). The secondary effluent is introduced into a sand filter before entering the ultrafiltration (UF) membrane (hollow fibre [HF] and spiral wound [SW]). After the UF process, the effluent is subjected to an activated-carbon adsorbent followed by reverse osmosis (RO) (advanced treatment). All effluents at different mixing ratios are used for an experimental programme of field irrigation. The UF process consists of two small-scale membrane treatment plants with a capacity of 12 $m^3\,d^{-1}$. The first UF unit is equipped with two 2 × 4 inch pressure vessels with a pressure resistance up to 150 psi. Each vessel holds two separation membranes (SW with 20 kDa cut-off, equivalent to a 0.01 μ separation rate, Nirosoft, Israel). The designed permeate capacity of the system is 0.5–0.8 $m^3\,h^{-1}$. This membrane can remove bacteria, suspended solids, turbidity agents, oil and emulsions. The second unit is equipped with two pressure vessels made by Vendor (AST Technologies model number 8000 WW 1000-2M, Israel) that houses the HF membranes with 100 kDa cut-off (Vendor, AST Technologies, Model no. 8000-WWOUT-IN-8080, Israel). The two units are designed to deliver 1.5 $m^3\,h^{-1}$. The RO system consists of a 1 × 4 inch pressure vessel constructed with composite material having a pressure resistance up to 400 psi.

The vessel holds two 4 inch special separation membranes (thin polyamide film with pH range 1–11, model BW30-4040 by DOW Filmtec, USA). A membrane anti-scaler (product NCS-106-FG) solution of phosphoric acid disodium salt is continuously dosed to the RO feed at a concentration of 4 mg L^{-1} in order to prevent deposition of divalent ions. The system is designed to remove major ions and heavy metals. The designed RO permeate capacity of the system is 0.45–0.50 $m^3\,h^{-1}$.

2.2. Methods

2.2.1. Micelle-clay complex preparation

The complex was prepared as described in [10]. Briefly, the micelle–clay complex was prepared by stirring 12 mM of ODTMA, or BDMHDA, with 10 g L^{-1} clay for 72 h. Suspensions were centrifuged for 20 min at 15000 rpm, supernatants were discarded, and the complex was lyophilized.

2.2.2. Batch experiments

Batch adsorption experiments were carried out for solutions of diclofenac potassium in the concentrations range 50–1000 mg L^{-1}. Experiments were performed in 250 mL Erlenmeyer flasks containing 0.500 g of either micelle–clay complex or active carbon; 100 mL of diclofenac potassium solutions with known initial concentration were then introduced to each flask. The flasks were shaken in an electric shaker for 3 h at room temperature; then the content of each flask was centrifuged for 5 min and filtered using a 0.45 μm Millipore filter. The equilibrium concentration of diclofenac potassium was then obtained spectrophotometrically. The kinetic study of the extent of adsorption was determined by measuring the absorbance over time of a 100 mL of solution containing 200 mg L^{-1} diclofenac potassium in 250 mL Erlenmeyer flasks added with 0.500 g of either micelle–clay complex or active carbon.

2.2.3. Column experiments

Column filter experiments were performed with 100:1 and 50:1 (w/w) mixtures of quartz sand and ODTMA– or BDMHDA–clay complex (20 cm layer) in a column of 25 cm length and 5 cm diameter. For both 100:1 and 50:1 mixtures the active component layer in the filter included either 6.5 or 13.0 g of the complex, corresponding to 2 or 4 g of ODTMA or BDMHDA cations, respectively. The bottom of the column was covered with a 3 cm layer of quartz sand. The quartz sand was thoroughly washed with distilled water and dried at 105 °C for 24 h. In some experiments the columns included 2 or 4 g of activated carbon mixed with sand as above. Solutions of varying diclofenac potassium concentrations (0.01, 0.1, 50, 100, 200, 300 and 1000 mg L^{-1}) were prepared by dilution of the stock solution with distilled water. These solutions were passed through the above columns. The flow rate was varied between 2.0 mL min^{-1} to 60 mL min^{-1}. Fractions were collected for assays of diclofenac potassium content.

2.2.4. HPLC–MS/MS measurements

Chromatographic separation was achieved on a Shimadzu prominence HPLC system equipped with: a degasser (DGU-20A_3), two solvent delivery units (LC-20 AD), an auto-sampler (SIL 20 ACHT) and a column oven thermostat operated at 30 °C (CTO-20 ASVP). Separation was performed using a Comosil column (5C_{18}-MS-II), 150 mm × 4.6 mm i.d., 5 μm particle size (Nacalai USA, Inc.). The mobile phase was 85% methanol and 15% water with 0.1% acetic acid at a flow rate of 1 mL min^{-1}. The sample

volume injected was 50 μL and the minimum concentration calibrated was 2 μ L^{-1}.

The HPLC system was coupled to a 3200 TRAP LC/MS/MS mass spectrometer (Applied Biosystems, MDS Sciex, USA) with an electrospray Turbo V ionization source. Acquisition was performed in the multiple reaction monitoring mode (MRM). Source conditions were established as follows: ion spray (IS) voltage, 5.0 kV (ESI^+), collision gas, medium, curtain gas, 50 kPa; ion source gas 1 (GS 1, nebulizer gas) and 2 (GS 2, turbo gas), 80, 90 kPa respectively, ion source temperature, 650 °C. High purity nitrogen (>98%) was produced by NitroGen 3G (Peak Scientific, USA) and used as desolvation, nebulization and collision gas. Optimization of MS/MS parameters was obtained by direct infusion, at 10 μL min^{-1}, of 100 ng mL^{-1} diclofenac standard solutions in 50% methanol aqueous solution.

Declustering potential (DP), collision energy (CE) and cell exit potential (CXP) voltages were established for each MRM transition. These values are displayed in Table 1. All data were acquired and processed using Analyst 1.5.1 software (USA).

Table 1. Diclofenac dependent MS/MS parameters optimized for the MRM acquisition mode.

MRM transition	DP (V)	CE (V)	CXP (V)
296/250	31	19	4
296/215	36	23	4

2.2.5. *Analysis of adsorption isotherms*

Equilibrium relationships between adsorbent and adsorbate were analysed by the linear form of the Langmuir adsorption isotherm [15]:

$$C_e/Q_e = 1/(k\,Q_{max}) + Ce/Q_{max} \quad (1)$$

in which C_e (mg L^{-1}) is the equilibrium concentration of diclofenac potassium, Q_e (mg g^{-1}) is the equilibrium mass of adsorbed diclofenac potassium per gram of complex or charcoal, k (L mg^{-1}) is the Langmuir binding constant, and Q_{max} (mg g^{-1}) is the maximum mass of diclofenac potassium removed per gram of complex.

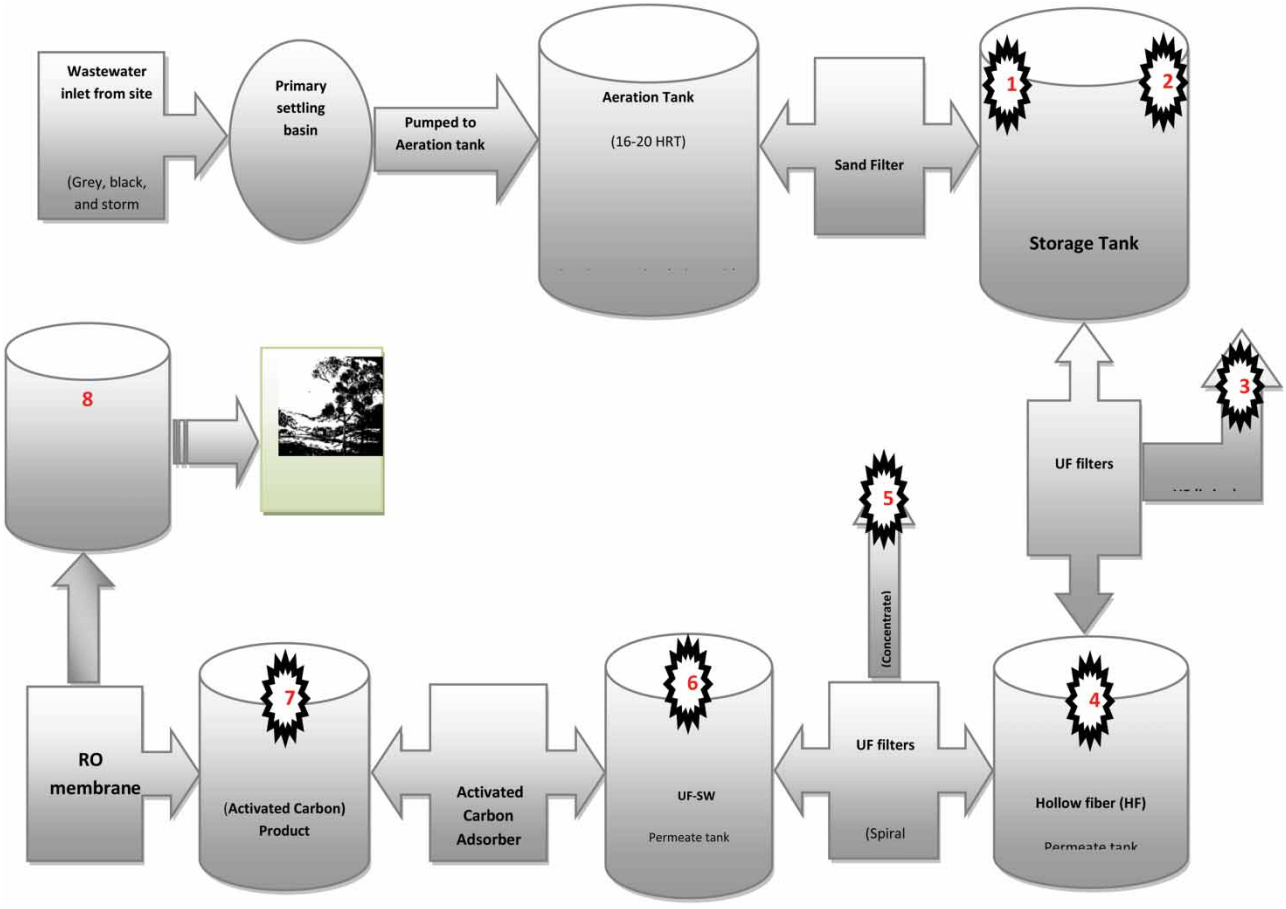

Figure 1. Flow diagram showing the process of the WWTP, which consists of HF-UF filters (hollow fibre) and SW-UF (spiral wound), activated carbon and RO filters. Sampling locations are indicated by the numbers.

2.2.6. *Preparation of sample and standards for stability and spiking studies*

(a) *Stock solution*. Five hundred millilitres of stock solution was prepared by dissolving 100 mg L^{-1} diclofenac potassium standard in acetonitrile in water (pH adjusted to 2.5) at a 65:35 ratio. This stock solution was used in (b).

(b) *Calibration curves*. The following solutions were prepared from the stock: 5, 10, 20, 40, 60, 80 and 100 mg L^{-1}.

(c) *Stability study in pure water*. For the stability study of diclofenac potassium in pure water, a 100 mg L^{-1} solution was used. The reaction progress was followed by HPLC.

(d) *Stability study in the presence of sludge.* The same diclofenac concentration as in (c) was used for the stability study of the active substance in the presence of sludge suspended in water. Samples at specific time intervals were collected and the liquid phase was extracted three times with ether.

(e) *Wastewater spiking and sampling.* An amount of 32 g of diclofenac potassium was dissolved in methanol and placed into a 500 L tank containing activated sludge effluent. Then seven wastewater samples were collected from different locations of the WWTP (Figure 1) using precleaned 500 mL amber glass bottles. Samples were kept on ice during transport to the laboratory. Once received, conventional wastewater parameters including temperature and pH were measured. The samples were then filtered and stored at 4 °C until extraction. These samples were collected for observing the efficiency of removal by UF (HF and SW) membranes, followed by activated carbon and RO membranes.

2.2.7. *Diclofenac potassium sample extraction*

A liquid–liquid extraction procedure was applied to the diluted solutions (used for the calibration curve) and wastewater samples by means of diethyl ether as solvent. Each sample was extracted three times. The ether extracts were combined, dried with anhydrous $MgSO_4$, filtered and evaporated. For HPLC-PDA analysis, the dried residue, after the ether evaporation, was dissolved in a mixture of acetonitrile:water (65:35, adjusted to pH 2.5) and then filtered through 0.45 mm filter before being injected to the HPLC apparatus.

2.2.8. *Chromatographic conditions*

After treatment by liquid–liquid extraction, the wastewater samples were analysed using HPLC-PDA. The optimal HPLC conditions found for the analysis of diclofenac potassium were: C-18 as the separation column; a mixture of water: acetonitrile (pH adjusted to 2.5 using dilute o-phosphoric acid) (35:65, v/v) as a mobile phase; a flow rate of 1.0 mL min^{-1}; UV detection at a wavelength of 289 nm.

3. Results and discussion

3.1. Spiking experiment

3.1.1. *Kinetic studies on the stability of diclofenac potassium in pure water and wastewater*

The monitoring of diclofenac potassium stability in pure water and in sludge revealed no degradation during more than one month of standing at ambient temperature. These findings indicate that diclofenac potassium is resistant to water hydrolysis and bacterial degradation.

3.1.2. *The efficiency of HF-UF, SW-UF, activated carbon and RO membranes in the removal of diclofenac*

Table 2 summarizes the results of the efficiency of HF-UF, SW-UF, activated carbon and RO membranes in removing diclofenac-from waste water after secondary treatment. The efficiency of the ultrafiltration process is about 30–75% (sample no. 4 and 5, see also Figure 1) in the removal of diclofenac from the effluent samples. On the other hand, both the activated carbon adsorbent and the RO membrane were significantly superior to UF in the removal of diclofenac potassium. A removal of about 95–100% was observed by both-filters (sample no. 7 and 8, see also Figure 1).

3.2. Batch adsorption

3.2.1. *Effect of contact time*

Figure 2 demonstrates a rapid decrease in the absorbance of diclofenac potassium in the presence of either charcoal or a micelle (ODTMA)–clay (montmorillonite) complex in dispersion. This indicates that most of the adsorption of diclofenac was accomplished within several minutes.

3.2.2. *Effect of initial concentration*

Table 3 summarizes the percentage removal of diclofenac as a function of initial concentration using ODTMA–clay complex and charcoal. The results indicate that for both adsorbents the per cent removal of diclofenac decreases as the initial concentration increases.

3.2.3. *Adsorption isotherms*

Figure 3 shows a linear relation between C_e/Q_e and C_e, indicating that the adsorption of diclofenac potassium by the micelle (ODTMA)–clay complex obeys the Langmuir isotherm model (Equation (1)). A similar pattern was seen for the case of charcoal.

The values of Q_{max} and k were determined from the slope and intercept in Figure 3. These values for the micelle–clay complex are 153.8 mg g^{-1} and 0.07 L mg^{-1}, respectively,

Table 2. Removal of diclofenac from wastewater by hollow fiber ultrafiltration (HF), spiral wound ultrafiltration (SW), activated carbon adsorbent and reverse osmosis.

Sample No. (see Figure 1)	Name of sample location	Concentration of diclofenac ± SD (mg L^{-1})
1	Blank (before addition of 32 g of diclofenac potassium)	0
2	Initial concentration of diclofenac K before running wastewater treatment plant	31.15 ± 0.01
3	Brine of AST-UF-HF	20.6 ± 0.1
4	Product of AST-UF-HF	10.3 ± 0.1
5	Nirosoft-UF (SW fibre) 'concentrate'	8.5 ± 0.1
6	Permeate of Nirosoft-UF (SW fibre)	3.7 ± 0.03
7	Product of activated carbon adsorbent	0.19 ± 0.01
8	Product of RO	0

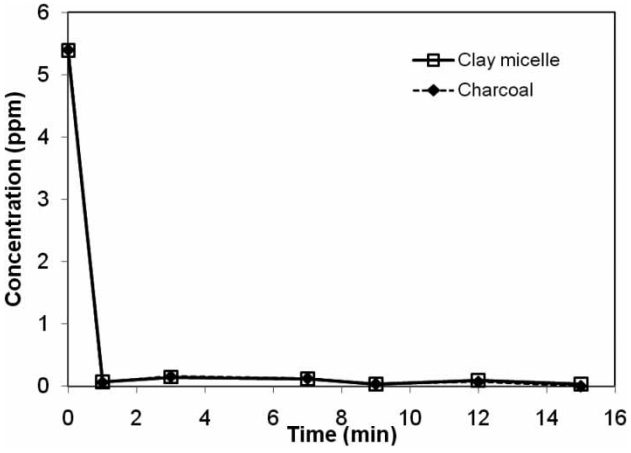

Figure 2. Adsorption of diclofenac on active carbon and micelle–clay complex as a function of time (min) at room temperature (25 °C).

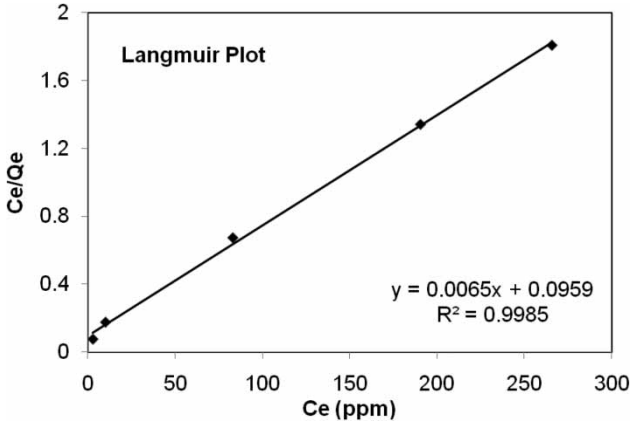

Figure 3. Langmuir plot for the adsorption of diclofenac by micelle (ODTMA)–clay complex. Conditions as in Table 3.

Table 3. Percentage removal of diclofenac from dispersions by micelle–clay, in which the surfactant was ODTMA, or activated carbon as a function of initial concentration after incubation for 3 h at a temperature of 27 °C.

Initial concentration (mg L^{-1})	Percentage removal (%)	
	Micelle–clay complex	Activated carbon
200	98.5 ± 0.5	100 ± 0.5
300	96.6 ± 0.6	99.8 ± 0.6
700	87.1 ± 1	93.2 ± 1
900	77.8 ± 1	–
1000	73.4 ± 1	78.6 ± 1

whereas the values for charcoal are 158.7 mg g^{-1} and 1.2×10^{-3} L mg^{-1}, respectively. The implication is that, on a w/w basis, there are about 3% more sites for adsorption of diclofenac on charcoal than on the micelle–clay complex, but the affinity coefficient of the complex is 58-fold higher than that of charcoal. Considering that the value of the cation exchange capacity of montmorillonite is 0.8 mmol g^{-1} and the fact that the clay comprises 0.692 of the weight of the micelle (ODTMA)–montmorillonite, it follows that the number of adsorption sites on the complex (which are positively charged) is 0.55 mmol g^{-1} complex. Considering the molecular weight of diclofenac, 295 Da, the above value is close to that deduced from Q_{max}, which is 0.52 mmol g^{-1}. A conversion of the value obtained for k (0.070 L mg^{-1}) yields 21,000 M^{-1}, which is about 10-fold higher than the values recorded in [12] for this complex, e.g. for acetochlor and alachlor, k = 1500 and 1000 M^{-1}, respectively.

It should be emphasized that the main reason for not seeing differences between the charcoal and by the micelle clay in the kinetics of diclofenac adsorption (Figure 2) is that the process involves centrifugation for several minutes, during which adsorption still proceeds.

3.3. *Filtration results*

3.3.1. *Estimates of filter capacity for high initial diclofenac concentrations*

In the first stage we obtained an estimate for the capacity of the filter, which included 13.0 g of the micelle (ODTMA)-clay complex with 4.0 g of ODTMA, to remove diclofenac from water. Figure 4 demonstrates that for an initial diclofenac concentration of 1000 mg L^{-1} all 20 portions, 50 mL each, resulted in complete removal of diclofenac.

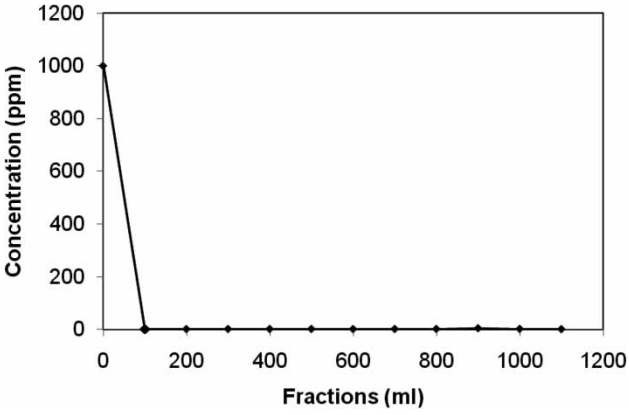

Figure 4. Concentration of emerging diclofenac vs fractions of diclofenac potassium at an initial concentration of 1000 mg L^{-1} and a volume of 1000 mL. Flow rate: 2 mL min^{-1}.

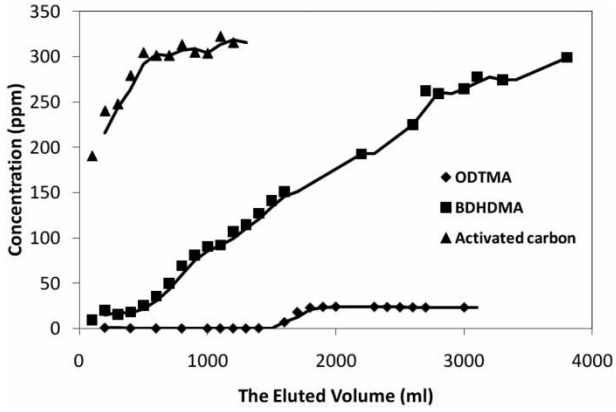

Figure 5. Emerging concentrations of diclofenac from filters including activated carbon or micelle–clay complexes in which the organic cation was ODTMA or BDMHDA. The filters included excess sand (100:1, w/w). The mass of the active ingredient, i.e. ODTMA, BDMHDA or activated carbon, was 2 g in all cases. T, 25 °C; flow rate, 20 mL min^{-1}; initial diclofenac potassium solution concentration, 300 mg L^{-1}.

This implies that at the end of this experiment the filter included 0.8 g of adsorbed diclofenac per 4.0 g of the organic cation ODTMA in the filter, or 20% w/w. After this stage several other solutions were added and their removal was monitored. The total amount of diclofenac retained by these additional solutions, at concentrations between 50 and 200 mg L^{-1}, was another 0.1 g, representing a removal $\geq$85%.

3.3.2. *Effect of flow rate*

The flow rate applied for the results in Figure 4 was rather low, 2 mL min^{-1}. We tested the effect of an increase in the flow rate from 2 mL min^{-1} to 20 mL min^{-1}. The outcome (not shown) was a moderate reduction (about 10%) in the capacity between the extreme cases (2 mL min^{-1} and 20 mL min^{-1}). In subsequent experiments, we employed a flow rate of 20 mL min^{-1} and more.

3.3.3. *Breakthrough curves: comparison between micelle–clay and activated carbon filters*

Figure 5 compares the efficiency and capacity of filters based on activated carbon and on two types of micelle–clay complexes, for a 300 mg L^{-1} solution of diclofenac potassium. The most efficient filter was the one composed of a mixture of 650 g of sand and 6.5 g of the micelle (ODTMA)–montmorillonite complex, or 2.0 g of ODTMA. For up to 1.5 L of eluent, this filter yielded complete removal of diclofenac, whereas, after elution of 3 L, the removal was maintained at 93%. The filter that included BDMHDA yielded 93% removal for the passage of less than 0.5 L, whereas, at 3 L, less than 10% of diclofenac was removed. Furthermore, the removal of diclofenac by BDMHA–clay complex was accompanied by the appearance of very turbid filtrates indicating the possible decomposition of the complex. For the activated carbon filters the removal efficiency was rather poor, consistent with the low capability of such filters in the removal of anionic and certain neutral pollutants [16–18].

Of note is the fact that the removal of several pollutants from dispersion or by filtration was either the same or more efficient by a micelle–clay complex based on BDMHDA than by a complex that included ODTMA [12]. This was attributed to interactions between the benzene rings of BDMHDA and the neutral or anionic pollutants considered, in accordance with a previous finding in the case of organo-clays [19]. The variance of the obtained results for diclofenac could be explained by the observation that binding of diclofenac with the micelle on the clay leads to a destabilization of the complex, thereby leading to the observed decomposition. The estimated weight of diclofenac that can be removed from a solution of 300 mg L^{-1} is about 1 g for the ODTMA–clay filter, or 50% of the weight of the organic cation ODTMA. The results of this work suggest that the removal of diclofenac by a micelle (ODTMA)–montmorillonite is promising. Hence, it was of interest to further examine this issue for diclofenac concentrations in the μg L^{-1} range.

3.3.4. *Filtration in the $\mu g L^{-1}$ range*

In these experiments we employed two systems, each consisting of two column filters in series. Each column included a mixture of 650 g sand with 6.5 g of the micelle (ODTMA)–montmorillonite complex or 2 g of ODTMA. This complex gave the best outcome in previous filtration experiments at large concentrations of diclofenac potassium. Experiments were carried out in four stages: (1) passage of 46 L of a solution with 118 μg L^{-1} of diclofenac; (2) passage of 45 L of a solution with 8 μg L^{-1} of diclofenac; (3) passage of 60 L of a solution with 80 μg L^{-1} of diclofenac; in these stages the flow rate was 30 mL min^{-1}; (4) passage of 70 L

Table 4. Filtration of diclofenac potassium in the $\mu g\ L^{-1}$ range. Emerging concentrations of diclofenac from two filters in series including a micelle–clay complex in which the organic cation was ODTMA.[a]

			Column 1		Column 2	
Initial concentration ($\mu g\ L^{-1}$)	Flow rate ($mL\ min^{-1}$)	Vol. (L)	Diclofenac ($\mu g\ L^{-1}$)	Removed (%)	Diclofenac ($\mu g\ L^{-1}$)	Removed (%)
118	30	20	0	100	0	100
118	30	46		100	0	100
8	30	71	0	100	0	100
8	30	91	0	100	0	100
82	30	101	0.2	99.8	0	100
82	30	116	0.4	99.6	0.2	99.8
82	30	151	0	100	0	100
80	60	221	0	100	0	100

[a]The filters included excess sand (100:1, w/w). The weight of the active substance, i.e. ODTMA, was 2 g per filter, and filtration was at room temperature. The estimated experimental uncertainty was $0.2\ \mu g\ L^{-1}$.

of a solution with $80\ \mu g\ L^{-1}$ of diclofenac at a flow rate of $60\ mL\ min^{-1}$. The results are shown in Table 4.

These results demonstrate that a filter which includes the micelle (ODTMA)–montmorillonite complex is very efficient in removing diclofenac from water. An underestimate of the capacity of the filter, for purifying water with an initial diclofenac concentration of $80\ \mu g\ L^{-1}$ at 99% removal, is obtained by counting the filtered volume of $8\ \mu g\ L^{-1}$ (stage 2) as one tenth of that at $80\ \mu g\ L^{-1}$ and considering the concentration of diclofenac in stage 1 as $80\ \mu g\ L^{-1}$. This estimate gives a capacity of 180 L per 2 g of ODTMA, or $90\ m^3\ kg^{-1}$ of ODTMA. A more realistic estimate may be that $100\ m^3$ of $80\ \mu g\ L^{-1}$ diclofenac (100 ppb of diclofenac potassium) can be purified by 1 kg of ODTMA. The actual estimate would be significantly larger when using larger filters. It can be argued that in addition to diclofenac potassium the water usually includes additional pollutants. In such cases the filtration can proceed in two stages. In the first stage a filter based on activated carbon will remove the majority of the neutral pollutants. This filter is not efficient in removing anionic pollutants, such as diclofenac. However the micelle–clay filter will remove these pollutants very efficiently in the second stage.

4. Conclusion

An advanced wastewater treatment plant utilizing UF, activated carbon and RO showed that UF is not efficient in removing the commonly used anti-inflammatory and analgesic diclofenac potassium from wastewater. However, activated carbon and RO were shown to be efficient. A filter that includes a micelle (ODTMA)–montmorillonite complex can purify water when this NSAID agent is present in the ppm or ppb range. The large effectiveness and removal capacity is due to a relatively high affinity of adsorption of the anionic diclofenac by the relatively large number of positively charged and hydrophobic sites of the micelle–clay complex based on ODTMA.

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