

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236922525>

# Efficiency of advanced wastewater treatment plant system and laboratory-scale micelle-clay filtration for the removal of...

Article in *Journal of Environmental Science and Health Part B* · September 2013

DOI: 10.1080/03601234.2013.781372 · Source: PubMed

CITATIONS

16

READS

258

9 authors, including:



**Mustafa Khamis**

Al-Quds University

57 PUBLICATIONS 1,167 CITATIONS

[SEE PROFILE](#)



**Sabino Aurelio Bufo**

Università degli Studi della Basilicata

201 PUBLICATIONS 1,446 CITATIONS

[SEE PROFILE](#)



**Rafik Karaman**

Al-Quds University

239 PUBLICATIONS 3,078 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



identification and characterization of glycoalkaloids in plants [View project](#)



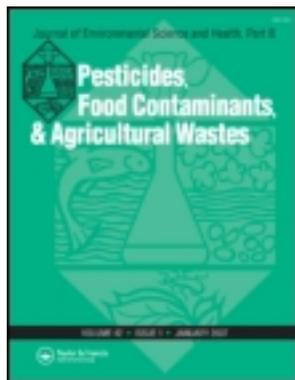
Design & Synthesis of Novel Prodrugs [View project](#)

This article was downloaded by: [Rafik Karaman]

On: 20 May 2013, At: 15:01

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lesb20>

### Efficiency of advanced wastewater treatment plant system and laboratory-scale micelle-clay filtration for the removal of ibuprofen residues

Samer Khalaf <sup>a b</sup>, Fuad Al-Rimawi <sup>a</sup>, Mustafa Khamis <sup>a</sup>, Dikla Zimmerman <sup>c</sup>, Uri Shuali <sup>c</sup>, Shlomo Nir <sup>c</sup>, Laura Scrano <sup>d</sup>, Sabino A. Bufo <sup>b</sup> & Rafik Karaman <sup>b e</sup>

<sup>a</sup> Department of Chemistry and Chemical Technology, Faculty of Science and Technology, Al-Quds University, Jerusalem, Palestine

<sup>b</sup> Department of Science, University of Basilicata, Potenza, Italy

<sup>c</sup> Department of Soil and Water Sciences, The R. H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, Israel

<sup>d</sup> Department of European Cultures (DICEM), University of Basilicata, Viale dell'Ateneo Lucano, Potenza, Italy

<sup>e</sup> Department of Bioorganic Chemistry, Faculty of Pharmacy, Al-Quds University, Jerusalem, Palestine

Published online: 20 May 2013.

To cite this article: Samer Khalaf, Fuad Al-Rimawi, Mustafa Khamis, Dikla Zimmerman, Uri Shuali, Shlomo Nir, Laura Scrano, Sabino A. Bufo & Rafik Karaman (2013): Efficiency of advanced wastewater treatment plant system and laboratory-scale micelle-clay filtration for the removal of ibuprofen residues, Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes, 48:9, 814-821

To link to this article: <http://dx.doi.org/10.1080/03601234.2013.781372>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Efficiency of advanced wastewater treatment plant system and laboratory-scale micelle-clay filtration for the removal of ibuprofen residues

SAMER KHALAF<sup>1,2</sup>, FUAD AL-RIMAWI<sup>1</sup>, MUSTAFA KHAMIS<sup>1</sup>, DIKLA ZIMMERMAN<sup>3</sup>, URI SHUALI<sup>3</sup>, SHLOMO NIR<sup>3</sup>, LAURA SCRANO<sup>4</sup>, SABINO A. BUFO<sup>2</sup> and RAFIK KARAMAN<sup>2,5</sup>

<sup>1</sup>Department of Chemistry and Chemical Technology, Faculty of Science and Technology, Al-Quds University, Jerusalem, Palestine

<sup>2</sup>Department of Science; University of Basilicata, Potenza, Italy

<sup>3</sup>Department of Soil and Water Sciences, The R. H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot, Israel

<sup>4</sup>Department of European Cultures (DICEM), University of Basilicata, Viale dell'Ateneo Lucano, Potenza, Italy

<sup>5</sup>Department of Bioorganic Chemistry, Faculty of Pharmacy, Al-Quds University, Jerusalem, Palestine

The efficiency of Al-Quds Waste Water Treatment Plant (WWTP), which includes sequential elements as activated sludge, ultrafiltration, activated carbon column and reverse osmosis, to remove spiked ibuprofen, a non steroid anti inflammatory drug (NSAID), was investigated. Kinetic studies in pure water and in the activated sludge indicated that the drug was stable during one month of observation. Besides, the overall performance of the integrated plant showed complete removal of ibuprofen from wastewater. Activated carbon column, which was the last element in the sequence before the reverse osmosis system, yielded 95.7% removal of ibuprofen. Batch adsorptions of the drug by using either activated charcoal or composite micelle-clay system were determined at 25°C and well described by Langmuir isotherms. Octadecyltrimethylammonium (ODTMA) bromide and montmorillonite were used to prepare the micelle-clay adsorbent, for which the adsorption kinetics are much faster than activated charcoal. Results suggest that integrating clay-micelle complex filters within the existing WWTP may be promising in improving removal efficiency of the NSAID.

**Keywords:** Ibuprofen, wastewater, activated carbon, micelle-clay composite, adsorption isotherms, adsorption kinetics.

## Introduction

Pharmaceuticals (antibiotics, anticonvulsants, antipyretics, cytostatic drugs, X-ray contrast media, hormones etc.) have been detected in sewage effluents, surface and ground water, and even in drinking water. Frequent occurrence of pharmaceuticals and other xenobiotic compounds in aquatic environments and drinking water has raised a concern about their potential effects on environment and human health. Some of the adverse health effects caused by pharmaceutical pollutants include aquatic toxicity, resistance induced to drugs used to control pathogenic bacteria, genotoxicity and endocrine disruption.<sup>[1–8]</sup>

Treatment of wastewater is performed to sustain and to protect the environment from pollution; in addition it enables finding alternative sources for fresh water, thus overcoming in part the increased scarcity of water in dry regions.

The level of treatment is still a controversial issue. Quite a few countries are moving rapidly towards advanced treatment of wastewater thus to carry out soil and aquifer protection from pollution. The major operations in wastewater treatment include the removal of suspended solids, dissolved solids, organic contaminants and pathogens. Usually, suspended solids are removed by filtration methods ranging from sand to membranes with nano-scale pores. Pathogens are removed by chlorination, ozonation, UV-disinfection, or membrane filtration with less than 20 kD cutoff porosity.<sup>[9–11]</sup>

Ibuprofen (structure 1 in Fig. 1) is a non-steroid anti-inflammatory drug (NSAID) with analgesic and antipyretic (fever-reducing) effects, and anti-inflammatory in higher doses. It is extensively used as non-prescription medicine, with an annual consumption of several hundreds of tons in developed countries.<sup>[12]</sup> Acidic pharmaceuticals such as ibuprofen, ketoprofen, naproxen, diclofenac, and indomethacin (with pKa values from 4.1 to 4.9) are not readily adsorbed by sludge in Waste Water Treatment Plants (WWTPs), and remain in the aqueous phase. Limited adsorption may occur at low pH values.<sup>[13–20]</sup>

Address correspondence to Rafik Karaman, Department of Bioorganic Chemistry, Faculty of Pharmacy, Al-Quds University, Jerusalem, Palestine; E-mail: dr\_karaman@yahoo.com

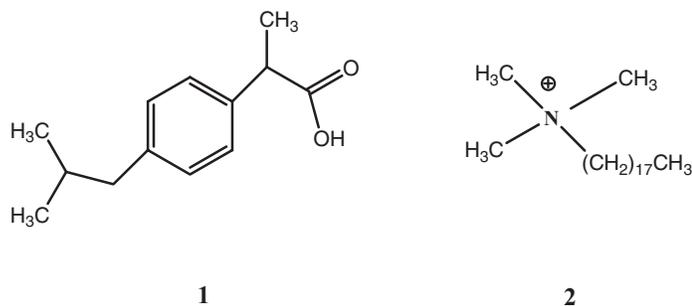


Fig. 1. Chemical structures for (1) ibuprofen and (2) ODTMA.

It has been reported that aerobic and anaerobic biodegradation are the most important processes for removal of pharmaceutical products from the dissolved phase. Ibuprofen is biodegraded faster in the warm season than in the cold season and it is more biodegradable in oxic than anoxic conditions.<sup>[21–26]</sup>

In this work the efficiency of Al-Quds University WWTP, which includes sequential elements as activated sludge, ultra-filtration, activated carbon column and reverse osmosis, to remove spiked ibuprofen, was investigated and compared to the effectiveness of a filtration column prepared in the Al-Quds laboratories using micelle-clay composite material.

## Materials and methods

### Chemicals and analytical methods

Ibuprofen pure standard (>99%), was obtained from Beir-Zeit Pharmaceutical Company (Palestine). Acetonitrile, methanol HPLC grade, orthophosphoric acid, magnesium sulfate, activated charcoal and octadecyltrimethyl ammonium (ODTMA) bromide were purchased from Sigma (Munich, Germany). The clay used was Wyoming Nantmorillonite SWY-2 obtained from the Source Clays Registry (Clay Mineral Society, Columbia, MO, USA). Quartz sand (grain size 0.8–1.2 mm) was obtained from Negev Industrial Minerals (Omar, Israel).

High Performance Liquid Chromatography (HPLC) system consisted of an Alliance 2695 HPLC (Waters, Milford, MA, USA), and a Waters Micromass<sup>®</sup> Masslynx<sup>™</sup> photo diode array detector (Waters 2996). Data acquisition and control were carried out using Empower<sup>™</sup> software from Waters. Analytes were separated on a 4.6 mm × 150 mm C18 XBridge<sup>®</sup> column (5 μm particle size) used in conjunction with a 4.6 mm × 20 mm XBridge<sup>™</sup> C18 guard column. Microfilters 0.45 μm (Acrodisc<sup>®</sup> GHP, Waters) were used. Single use C<sub>18</sub> (1 g–6 mL) cartridges from Waters were adopted. The C18 cartridges were preconditioned by passing first 10 mL of water through the cartridge and then 10 mL of acetonitrile. The cartridges were then air-dried. Several aqueous solutions (from 1.0 to 50.0 mg L<sup>-1</sup>)

of ibuprofen (10 mL) were passed through the cartridge. Adsorbed ibuprofen was eluted from the cartridge using 10 mL of acetonitrile. Afterwards, 20 μL of the eluate was injected into the HPLC and analyzed. HPLC conditions were: flow rate = 1.0 mL min<sup>-1</sup>, isocratic mobile phase: 50% of 0.07% phosphoric acid aqueous solution + 50% acetonitrile, detector wavelength = 220 nm. Peak areas vs. concentration of ibuprofen were plotted and the calibration curve was obtained with a determination coefficient (R<sup>2</sup>) of 0.9966.

For the determination of ibuprofen residues at level of μg L<sup>-1</sup>, LC-MS micro-analysis was performed using Agilent 1200 Rapid Resolution LC system (Agilent Technologies Inc., Santa Clara, CA, USA). Chromatographic separations was carried out by means of Gemini Hexyl-Phenyl HPLC column 2 × 150 mm, particle size 3 μm (Phenomenex Inc., Torrance, CA USA), upon isocratic elution using 20% water added with 1.5% AcOH and 80% acetonitrile added with 0.05% AcOH. Flow rate = 0.24 mL min<sup>-1</sup>, column temperature = 40°C, injection volume = 50 μL. The mass spectrometry section was the Agilent 6410 triple quad mass selective detector equipped with an electrospray ionization source. The mass spectrometer was operated in negative ionization mode; capillary voltage 3500 V; drying gas (nitrogen) temperature and flow 350°C and 10 L min<sup>-1</sup>, respectively; nebulizer pressure 35 psi, nitrogen (99.999%) was used as collision gas. The LC-MS system was controlled and data were analyzed using Mass Hunter software (Agilent Technologies Inc.). Quantitative analysis of ibuprofen was performed in multiple reaction monitoring (MRM) mode. Labeled ibuprofen was used as an internal standard, and ions at m/z 205–161 and 208–164 for ibuprofen and labeled-ibuprofen, respectively, were detected and quantified.

### Ibuprofen stability and WWTP removal efficiency

The WWTP of Al-Quds University (Campus of Abu-Dies, Jerusalem) has been described elsewhere.<sup>[27–29]</sup> Briefly, it consists of a primary treatment (two stage primary settling basin), secondary treatment (activated sludge with a hydraulic retention time of 16–20 hours, coagulation and chlorination). Then the secondary effluent is introduced into the sand filter before entering the ultra-filtration (UF) membranes (hollow fiber and spiral wound). After the UF process, the effluent undergoes activated carbon adsorption followed by reverse osmosis (advanced treatment). In Fig. 2 the flow drawing of wastewater treatment process has been described. A mixture of all effluents is used for irrigation of crops in the campus field.

Prior to perform any other experiment, the stability of ibuprofen dissolved in pure water and in the activated sludge collected from the WWTP was determined to ascertain if hydrolysis or bio-degradation reactions were going to occur before the filtration stages. For this reason, samples were collected at specific times from 50 mg L<sup>-1</sup>

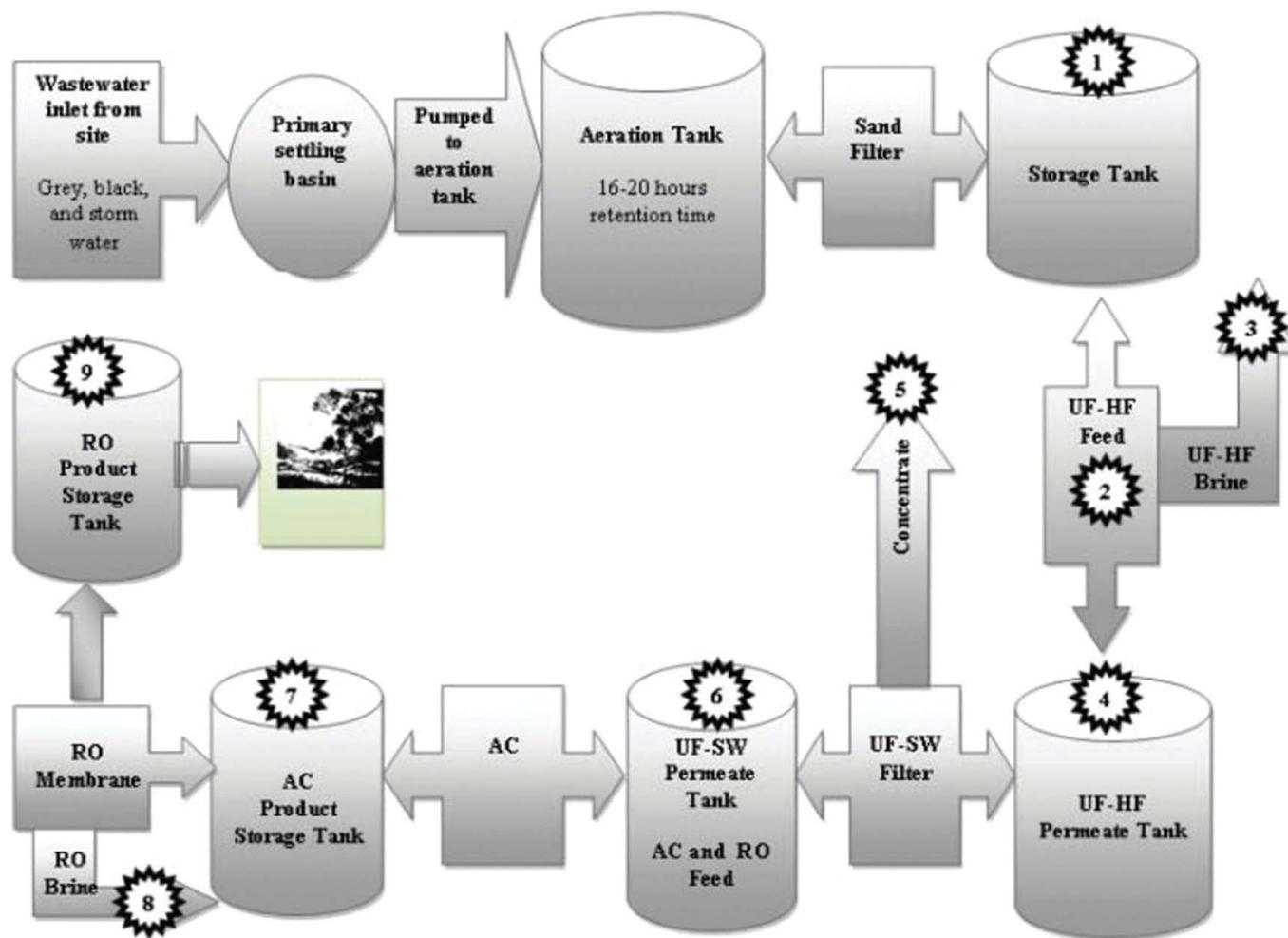


Fig. 2. Flow drawing of WWTP at Al-Quds University (color figure available online).

pure water solution of ibuprofen and analyzed by HPLC. In the second trial the activated sludge was spiked with the same quantity of the drug and aeration was permitted to preserve the bacterial growth in the mixture. The concentration of ibuprofen at each time interval was determined using the calibration curve and the percentage of degraded ibuprofen was calculated as the difference from the initial concentration.

The efficiency of the different filtration stages, hollow fiber (UF-HF), spiral wound (UF-SW), activated carbon (AC) and reverse osmosis (RO) for the removal of ibuprofen from wastewater was studied by spiking ibuprofen in the storage tank of the WWTP at a concentration of  $40 \text{ mg L}^{-1}$  (by dissolving 25 g of ibuprofen in the storage tank containing 625 L of wastewater). Samples were taken from the following points of WWTP (Fig. 2): (1) storage tank (before running any filtration process); (2), (3), and (4) feed, brine and permeate from the UF-HF membrane, respectively; (5) and (6) concentrated and permeate from the UF-SW membrane, respectively; (7) AC permeate; (8) RO brine; (9) RO final product. All these samples were analyzed as described in the section "Chemicals and Analytical Methods."

### Micelle-clay complex preparation

The complex was prepared as described elsewhere.<sup>[30–32]</sup> Briefly, the micelle-clay complex was obtained by stirring 12 mM of ODTMA with  $10 \text{ g L}^{-1}$  clay for 72 h. The suspension was centrifuged for 20 min at 15,000 g, the supernatant was discarded, and the complex was lyophilized.

### Batch adsorption isotherms

Adsorption capacity of the micelle-clay complex was studied and compared to the adsorption effectiveness of activated charcoal. The equilibrium relationships between adsorbents (clay micelle complex and activated charcoal) and ibuprofen were described by adsorption isotherms obtained determining the percentage of drug retained by each adsorbent from aqueous solutions at different concentrations (50, 100, 200, 500 and  $1000 \text{ mg L}^{-1}$ ). The following procedure was applied: 100 mL from each solution were transferred to 200 mL Erlenmeyer flask, 0.5 g of the micelle-clay complex, or charcoal, were then added into the flask. The flask was shaken for 180 minutes. The equilibrium was

ascertained analyzing the solution at different times after 0.45  $\mu\text{m}$  membrane filtration until the concentration of the drug remained constant. The experiment was repeated at two pH values, 4 and 8. In the last case pH was adjusted adding drop by drop a 1M solution of sodium hydroxide.

Adsorption isotherms were well described by the linear form of the Langmuir Eq. 1.<sup>[27–29]</sup>

$$C_e/Q_e = 1/(kQ_{\max}) + C_e/Q_{\max} \quad (1)$$

where  $C_e$  is the equilibrium concentration of ibuprofen in the liquid phase ( $\text{mg L}^{-1}$ ),  $Q_e$  ( $\text{mg g}^{-1}$ ) is the mass of ibuprofen adsorbed per gram of complex or charcoal,  $k$  is the Langmuir binding-strength coefficient ( $\text{L mg}^{-1}$ ), and  $Q_{\max}$  is the maximum mass of drug retained per gram of complex or charcoal.

### Column experiments

Column filter experiments were performed with 100:1 (wt wt<sup>-1</sup>) mixtures of quartz sand and ODTMA-clay complex (20 cm layer) in a column of 25 cm length and 5 cm diameter, which included 6.5 g of complex, corresponding to 2 g of the cation ODTMA. The bottom of the column was covered with 3 cm layer of quartz sand. The quartz sand was thoroughly washed by distilled water before its use and dried at 105°C for 24 h. A similar column was prepared including 2 g of activated carbon mixed with sand as above. Solutions of ibuprofen at different concentrations (from 0.01 to 16.7  $\text{mg L}^{-1}$ ) were passed through the columns. The flow rate was varied between 30.0  $\text{mL min}^{-1}$  to 60  $\text{mL min}^{-1}$ . The eluted fractions were collected and analyzed for ibuprofen concentration. All experiments were conducted in triplicates.

### Kinetics of column filtration

The adsorption and convection in the column can be described by Eq. 2.<sup>[34]</sup>

$$dC(X, t)/dt = -v \cdot \partial C/\partial X - C_1 \cdot C(X, t)R(X, t) + \alpha \cdot D_1 (R_o - R(X, t)) \quad (2)$$

A column of length  $L$  is filled with material whose adsorbing sites have initially a molar concentration  $R_o$ , changing later into  $R(X, t)$ . The top and bottom coordinates of the filter are  $X = 0$  and  $X = L$ , respectively. We consider that the pollutant concentration at the inlet ( $C_o$ ) is independent by the time, i.e.  $C(X, t) = C_o$ ,  $X \leq 0$ , where  $t$  indicates the time.

The kinetic parameters are  $C_1$  ( $\text{M}^{-1}\text{min}^{-1}$ , forward rate constant of adsorption),  $D_1$  ( $\text{min}^{-1}$ , rate constant of desorption),  $v$  (flow velocity);  $\alpha$  ( $<1$ ) degree of hysteresis, which was not considered in this case. For the numerical calculations a FORTRAN program was adopted.<sup>[34]</sup>

## Results and discussion

### Stability of ibuprofen in pure water and in the presence of activated sludge

Stability studies of ibuprofen in pure water were carried out at 25°C collecting and analyzing samples at different times from a solution of 50  $\text{mg L}^{-1}$  stored in the darkness for 30 days. Results showed that ibuprofen was stable during the whole month, i.e. no degradation was detected in pure water.

The stability of ibuprofen was also ascertained in the wastewater containing activated sludge with total plate count (TPC) = 25  $10^7$  Cfu 100  $\text{mL}^{-1}$  at 25°C for 30 days. Ibuprofen was also stable in these conditions; no degradation was observed.

### Ibuprofen removal efficiency by the WWTP filtration stages

The efficiency of the wastewater treatment plant (WWTP) at Al-Quds University for ibuprofen removal was studied and reported in Table 1. In the permeate of the UF-HF system 59.8% of the spiked quantity was removed, getting 94.7% in the permeate of UF-SW stage and 98.8% in the water sampled after the AC stage. The complete removal (99.9%) of ibuprofen was achieved after passing through the RO membrane. Hence, AC adsorption and RO system were crucial components of Al-Quds WWTP for removal of ibuprofen in an environmentally acceptable amount. The efficiency of the treatment plant was permitting a healthy

**Table 1.** Removal of ibuprofen by ultra-filtration membranes (UF-HF and UF-SW), activated carbon (AC) and reverse osmosis (RO) in the Al-Quds University WWTP (Figure 2).

No.	Sample location	Ibuprofen concentration ( $\text{mg L}^{-1}$ )		Cumulative removal%	
		Means of 3 replicates	$\pm SD$	Means of 3 replicates	$\pm SD$
1	Concentration determined in the storage tank after the drug addition (40 $\text{mg L}^{-1}$ )	39.83	2.65	—	—
2	UF-HF Feed	39.17	3.72	—	—
3	UF-HF Brine	39.23	3.19	—	—
4	UF-HF Permeate	16.13	6.89	59.76	16.57
5	UF-SW Concentrate	13.57	10.80	—	—
6	UF-SW Permeate	2.17	1.93	94.72	4.42
7	AC Permeate	0.49	0.30	98.77	0.74
8	RO Brine	0.37	0.41	—	—
9	RO Permeate	0.04	0.04	99.89	0.12

purification and recycling of wastewater, but the drug was mostly accumulated in the concentrate and brine of the ultra-filtration system and in the brine of RO process due to the chemical persistence of ibuprofen and its recalcitrant reaction to the microbial attack.

#### Adsorption of ibuprofen into the micelle- clay complex and activated charcoal

We focus here about a relatively novel tool for removal of pharmaceuticals from wastewater by using a micelle-clay sorbent. The micelle-clay composite, used in this study, is positively charged, has great surface area and includes large hydrophobic domains. It was shown by X-ray diffraction, electron microscopy and adsorption experiments that the structure of micelle-clay complex is different from that of an organo-clay complex formed by the adsorption of monomers of the same organic cation ODTMA (structure 2 in Fig. 1).<sup>[30]</sup> Micelle-clay composites have already been proven useful in the removal of about 20 neutral and anionic pollutants.<sup>[31–34]</sup> The complex prepared was possessing excess of positive charge and including relatively large hydrophobic regions, thus being particularly capable of binding negatively charged organic molecules.<sup>[30–32]</sup>

The adsorption of ibuprofen at five concentrations (50, 100, 200, 500, and 1000 mg L<sup>-1</sup>) into the clay micelle complex was determined and compared to adsorption into activated charcoal. In both cases adsorption parameters were calculated by Eq. 1. The  $C_e/Q_e$  vs.  $C_e$  values were plotted as shown in Fig. 3. The relationship between  $C_e/Q_e$  and  $C_e$  is

linear for both the clay micelle complex and activated charcoal with the determination coefficient  $R^2$  resulting larger than 0.99 in both cases.

Table 2 provides the values of the two parameters  $Q_{max}$  and  $k$  for the adsorption of ibuprofen into the micelle-clay complex and activated charcoal from solutions at pH = 4. Results demonstrate that at the steady state the two tested adsorbents, clay micelle complex and activated charcoal, have the same efficiency for the removal of ibuprofen: both  $Q_{max}$  and  $k$  values are comparable.

The value of  $Q_{max}$  can be related to the number of available charged sites of the micelle-clay complex. Considering that the clay/micelle-clay weight ratio is 4.5:6.5 (wt wt<sup>-1</sup>) and the cation exchange capacity of montmorillonite is 0.8 mmol g<sup>-1</sup>,<sup>[32]</sup> the number of adsorption sites of the complex (which are positively charged) is 0.55 mmol g<sup>-1</sup>. From the molar mass of ibuprofen (206.28 g mol<sup>-1</sup>) and the value of  $Q_{max}$  given in Table 2 (61.0 mg g<sup>-1</sup>) it is easily to calculate for ibuprofen a value of *ca.* 0.3 mmol g<sup>-1</sup>, which is approximately one half of the charged sites per g of the complex. In a recent analysis of filtration results of the anionic herbicide sulfentrazone<sup>[34]</sup> a similar value was ascertained. A conversion of the Langmuir binding-strength coefficient  $k$  obtained for ibuprofen (0.63 L mg<sup>-1</sup>) yields 130,000 M<sup>-1</sup>, which is similar to the value calculated for sulfentrazone (120,000 M<sup>-1</sup>).<sup>[34]</sup>

Ibuprofen pKa is 4.4 and the pH measured in the pure water spiked sample was 4.0. It is easily to calculate that the unmodified aqueous solution of the drug approximately contained 29% of the anionic form and 71% of the acidic

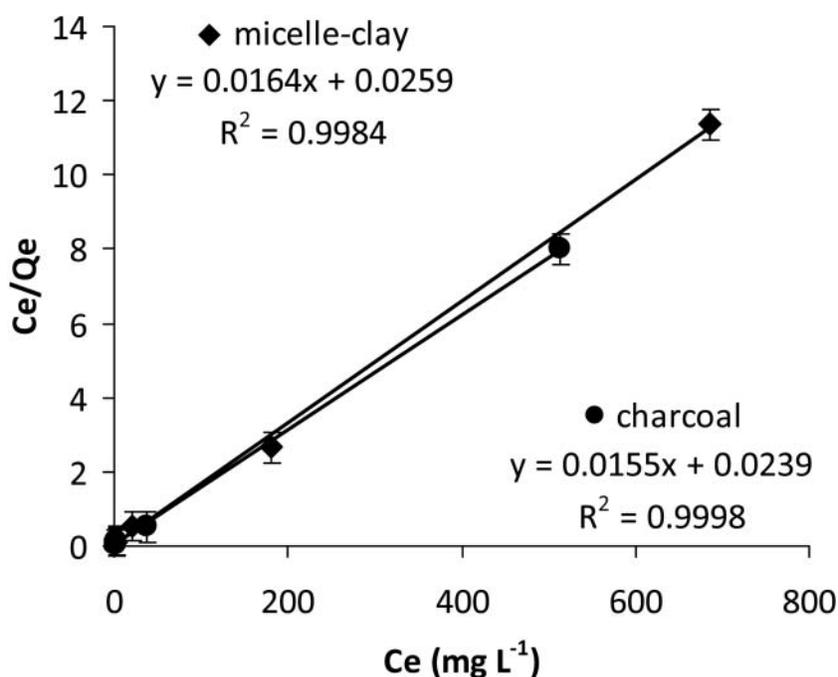


Fig. 3. Langmuir isotherms for the removal of ibuprofen either by micelle- clay complex or activated charcoal. Value reported are the means of three replicates.

**Table 2.** Langmuir adsorption parameters ( $k$  and  $Q_{\max}$ )\* for ibuprofen on micelle (ODTMA)-clay complex and activated charcoal.

Adsorbent	$k$ ( $L\ mg^{-1}$ )	$Q_{\max}$ ( $mg\ g^{-1}$ )
Micelle-clay complex	$0.63 \pm 0.03$	$61.0 \pm 0.68$
Activated charcoal	$0.65 \pm 0.03$	$64.5 \pm 0.35$

\*Values of  $k$  and  $Q_{\max}$  are presented as mean  $\pm$  standard deviation (three replicates)

non-ionized form. At pH 4 the kinetics of batch adsorption into the micelle-clay complex was relatively fast with a half-time of 4.24 min calculated for the more diluted tested solution, containing 5 mg of ibuprofen and 0.5 g of the adsorbent micelle-clay complex in 100 mL of water. In these conditions the amount of ibuprofen adsorbed at steady state was 59% of the initial concentration in the liquid phase. Besides, at pH 8.0 ibuprofen is completely transformed in the ionized form, 90% of which was retained into the adsorbent with a half-time of 2.8 min.

The contribution of the anionic fraction to the retention into the adsorption sites of micelle-clay complex can be calculated as 90% of its fraction in the solution; at pH 4 this fraction is 29% of total free compound concentration, i.e. its contribution is 26% of the total adsorbed, whereas the neutral fraction supplies 33% of the adsorbed compound. The implication is that 46% of neutral fraction was removed from the solution vs. 90% of the anionic form. According to the Langmuir equation the ratio between the fraction retained and the free one, for a given concentration of adsorbing sites is approximately proportional to the product of binding-strength coefficient multiplied by the concentration of total binding sites. This ratio is 9 for the anionic form and 0.88 for the neutral form. The implication is that the affinity of adsorption to the micelle-clay complex is about 10-fold larger in the case of the anionic form.

The adsorption of ibuprofen into the activated charcoal at pH 8.0 was as effective as the adsorption into the micelle-clay complex with a half-time of 58 min. The total adsorbed percentage was about 98%, but the steady state was reached after two hours. This means that the adsorption capacity of ibuprofen into the clay micelle complex and activated charcoal was comparable, but the adsorption of ibuprofen into the clay micelle complex was faster than the activated charcoal.

### Removal through filtration

Experiments using column filter ( $20 \times 5$  cm) were performed with 100/1 (wt wt<sup>-1</sup>) mixtures of quartz sand and ODTMA-clay complex or activated carbon. Ibuprofen solutions ranging from 3.9 to 16.7 mg L<sup>-1</sup> were eluted through the micelle-clay column at flow rates of 30 and 60 mL min<sup>-1</sup>. A solution of 15.7 mg L<sup>-1</sup> at flow rate of 60 mL min<sup>-1</sup> was eluted as control test using either the

micelle-clay or the activated carbon column. Results are presented in Table 3 and indicate an acceptable efficiency of micelle-clay complex for the removing of pollutant at lower initial concentration, but the retention of ibuprofen in the column was dramatically diminishing when the eluted volume was major than 7 L and the flow rate was increased from 30 to 60 mL min<sup>-1</sup>. Nevertheless, an appreciable advantage in removing ibuprofen by the micelle-clay filter over the activated carbon was maintained in the control trial.

Despite that Figure 3 and Table 2 point out that parameters of adsorption isotherms were similar for adsorption by the micelle-clay complex or activated carbon, the adsorption kinetics was about 20 times faster in the case of the micelle-clay complex than activated carbon. Hence, it might be expected that the micelle-clay filter would be more efficient in the removal of ibuprofen from water than the activated carbon.

To verify the effect of the cumulative volume eluted through the micelle-clay/sand column we performed a new test using ibuprofen concentration at  $\mu\text{g L}^{-1}$  level, which was expected to avoid the saturation of sorption sites. The experiment was performed in duplicate eluting a solution of 109.8  $\mu\text{g L}^{-1}$  ibuprofen through two filters joined in series at a flow rate of 50 mL min<sup>-1</sup>. Thus, for each volume passed two data points were provided, the concentration of

**Table 3.** Removal of ibuprofen at different concentrations and flow rates by column filtration including either a micelle-clay complex or activated carbon mixed with excess sand at 1:100 (wt wt<sup>-1</sup>).

Eluted volume (L)	Concentrations* ( $mg\ L^{-1}$ )	Experimental percentages**	Calculated percentages#
Initial concentration: 3.9 mg L <sup>-1</sup> ; Flow rate: 30 mL min <sup>-1</sup>			
1	0.01	99.7	99.7
2	0.01	99.7	99.5
3	0.02	99.5	99.2
Initial concentration: 15.7 mg L <sup>-1</sup> ; Flow rate: 60 mL min <sup>-1</sup>			
3.6	1.7(6.1) <sup>§</sup>	89.2(61.1) <sup>§</sup>	89.9
7.2	3.3(6.6) <sup>§</sup>	79.7(59.2) <sup>§</sup>	77.2
14.4	10.9(8.0) <sup>§</sup>	29.2(48.3) <sup>§</sup>	36.9
Initial concentration: 16.7 mg L <sup>-1</sup> ; Flow rate: 60 mL min <sup>-1</sup>			
3.6	1.6	90.6	89.8
9	3.6	78.1	68.8
10.8	5.8	65.5	59.5
12	8.2	50.7	49.5
14.4	11.6	30.7	36.6

\*Concentrations in the eluted volumes; means of three replicates.

\*\*Percentages retained into the column per each eluted volume; means of three replicates.

<sup>§</sup>Values in brackets refer to the activated carbon filter.

#Calculations were made according to Eq. 2; values of parameters employed:  $R_0 = 0.013\ M$ ;  $C_1 = 150\ M^{-1}\text{min}^{-1}$ ;  $D_1 = 0.005\ \text{min}^{-1}$ .

**Table 4.** Removal of ibuprofen through filtration (initial concentration  $109.8 \mu\text{g L}^{-1}$ ) by two columns in series, each including a mixture of a micelle-clay complex with excess sand, experimental and predicted results. Flow rate =  $50 \text{ mL min}^{-1}$ ; conditions and the parameters as in table 3.

<i>V (L)</i>	<i>Emerging concentration (<math>\mu\text{g L}^{-1}</math>)</i>	<i>Removed exp. (%)</i>	<i>Removed calc. (%)</i>
<i>Column 1</i>			
6	2.7	97.5	93.5
9	2.3	97.9	90.3
15	5.3	95.2	82.6
30	41.6	62.1	60.1
66	86.7	21.0	19.4
<i>Column 2</i>			
6	1.4	98.7	99.8
9	0.32	99.7	99.6
15	0.22	99.8	98.6
30	0.5	99.5	93.7
66	11.9	89.1	64.5

the drug emerging from the first filter and the concentration eluting from the second one.

The experimental data were compared to those calculated by employing Eq. 2. This equation ignores both molecular diffusion and mechanical dispersion for the flow through the filter, which can be justified when solute transport is dominated by adsorption rather than diffusion and dispersion.<sup>[34]</sup> In these calculations we fixed the value of  $R_0$ , total molar concentration of adsorbing sites in the filter, from the value of  $Q_{\text{max}}$ , which was obtained by the Langmuir isotherm in Table 2. The software used for calculations required to find the best fit between the experimental and calculated values by adjusting the parameters C1 and D1 in Eq. 2. The comparison between experimental and calculated results is reported in Table 4. A reasonably good correlation ( $R^2 = 0.9876$ ) was achieved reporting the experimental vs. the calculated values obtained by the elution through the first column. The value of the determination coefficient diminished to 0.9580 for the correlation of data obtained for the second column. Nevertheless, both the values of  $R^2$  indicate a reasonably acceptable prediction obtained by means of Eq. 2.

Results reported in Table 4 demonstrate the effect of doubling the length of the filter, after passing through column 2 on the reduction of the eluted concentration of ibuprofen, or alternatively, on increasing the percentage of its removal. Thus doubling the length of the filter resulted in enhancing its retention capacity per weight unit of the micelle-clay complex. The effectiveness of the filtration column can be easily predicted by Eq. 2, the parameters of which were obtained by the coefficients of Eq. 1 using a simple software for the calculations.

## Conclusion

In this study an acidic pharmaceutical, ibuprofen, was found to be stable in wastewater (for 30 days). Therefore, it was necessary to find a method for the removal of this or similar pharmaceuticals from wastewater. An advanced wastewater treatment plant sited in the campus of Al-Quds University (Palestine) utilizing ultra-filtration, activated carbon and reverse osmosis showed that the two ultra-filtration stages employed (UF-HF and UF-SW) were not sufficient in removing the added ibuprofen to a safe level, whereas by using AC and RO adequate results were obtained. Adsorption studies on micelle (ODTMA)-clay complex and charcoal revealed that under steady state conditions both adsorbents yielded similar efficiency for removal of ibuprofen. However, the kinetics of adsorption was much faster using the micelle-clay complex than the activated charcoal. This outcome resulted in a more efficient removal of ibuprofen through filtration by means of a micelle-clay column than by an activated carbon filter.

Finally, obtained results may suggest that integrating clay-micelle complex filters within the existing advanced waste water treatment system may be promising in improving removal efficiency of recalcitrant pharmaceutical residues. The more adequate dimensions of filters can be easily calculated by using a simple algorithm with the help of a homemade software.

## Acknowledgments

Bir-zeit Pharmaceutical Co. is thanked for the supply of ibuprofen. The work was supported by a generous grant from Sanofi Pharmaceutical Company (France).

## References

- [1] Daughton, C.G.; Ternes, T.A. Pharmaceuticals and personal care products in the environment: agents of subtle change? *Environ. Health Perspect.* **1999**, *107* (6), 907–938.
- [2] Heberer, T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicol. Lett.* **2002**, *131*, 5–17.
- [3] Ternes, T.A. Occurrence of drugs in German sewage treatment plants and rivers. *Water Res.* **1998**, *32*, 3245–3260.
- [4] Kummerer, K. Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources- a review. *Chemosphere* **2001**, *45*, 957–969.
- [5] Halling-Sorensen, B.; Nielsen, N.; Lansky, P.; Ingerslev, F.; Hansen, L.; Lutzhoft, H. Occurrence, fate and effects of pharmaceutical substances in the environment - a review. *Chemosphere* **1998**, *36*, 357–394.
- [6] Kolpin, D.W.; Furlong, E.; Meyer, M.; Thurman, E.; Zaugg, S.; Barber, L.; Buxton, H. Pharmaceuticals, hormones and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. *Environ. Sci. Technol.* **2002**, *36* (6), 1202–1211.
- [7] Schwarzenbach, R.; Escher, B.; Fenner, K.; Hofstetter, T.; Johnson, C.; Gunten, U.; Wehrli, B. The challenge of micropollutants in aquatic systems. *Science* **2006**, *313*, 1072–1077.

- [8] Kummerer, K. The presence of pharmaceuticals in the environment due to human use—present knowledge and future challenges— a review. *J. Environ. Manage.* **2009**, *90*, 2354–2366.
- [9] United States Environmental Protection Agency (USEPA). *Wastewater Treatment Manuals: Primary, Secondary and Tertiary treatment*; Author: Washington, DC, 1997.
- [10] USEPA. *Primer for Municipal Wastewater treatment systems*; Author: Washington, DC, 2004.
- [11] Acero, J.; Benitez, F.; Leal, A.; Real, F.; Teva, F. Membrane filtration technologies applied to municipal secondary effluents for potential reuse. *J. Hazard. Mater.* **2010**, *177*, 390–398.
- [12] Mycek, M.J.; Harvey, R.A.; Champe, P.C.; Fisher, B.D. *Lippincott's Illustrated Reviews: Pharmacology, second ed.*; Lippincott Williams & Wilkins: Philadelphia, 2000, 401–418.
- [13] Ashton, D.; Hilton, M.; Thomas, K.V. Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom. *Sci. Total Environ.* **2004**, *333*, 167–184.
- [14] Carballa, M.; Omil, F.; Lema, J.M.; Llompert, M.; Garcia-Jares, C.; Rodriguez, I.; Gomez, M.; Ternes, T. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Res.* **2004**, *38*, 2918–2926.
- [15] Heberer, T.; Reddersen, K.; Mechliniski, A. From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas. *Water Sci. Technol.* **2002**, *46*, 81–88.
- [16] Kümmerer, K. (Ed.) *Pharmaceuticals in the Environment*, 2nd Ed. Springer: Berlin, 2004; 1–527.
- [17] Quintana, J.B.; Reemtsma, T. Sensitive determination of acidic drugs and triclosan in surface and wastewater by ion pair reversed-phase liquid chromatography/tandem mass spectrometry. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 765–774.
- [18] Stumpf, M.; Ternes, T.A.; Haberer, K.; Seel, P.; Baumann, W. Determination of pharmaceuticals in sewage plants and river water. *Vom Wasser* **1996**, *86*, 291–303 (in German).
- [19] Buser, H.R.; Poiger, T.; Mueller, M.D. Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. *Environ. Sci. Technol.* **1999**, *33*, 2529–2535.
- [20] Metcalfe, C.D.; Koenig, B.D.; Bennie, D.T.; Servos, M.; Ternes, T.A.; Hirsch, R. Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. *Environ. Toxicol. Chem.* **2003**, *22*, 2872–2880.
- [21] Stumpf, M.; Ternes, T.A.; Haberer, K.; Baumann, W. Isolation of ibuprofen metabolites and their importance as pollutants of the aquatic environment. *Vom Wasser* **1998**, *91*, 291–303 (in German).
- [22] Halling-Sorensen, B.; Nors Nielsen, S.; Lanzky, P.F.; Ingerslev, F.; Lützhøft, H.; Jørgensen, S.E. Occurrence, fate and effects of pharmaceutical substances in the environment—a review. *Chemosphere* **1998**, *36*, 357–393.
- [23] Higson, F.K. Microbial degradation of biphenyl and its derivatives. *Adv. Appl. Microbiol.* **1992**, *37*, 135–164.
- [24] Kepp, D.R.; Siedelmann, U.G.; Tjornelund, J.; Hansen, S.H. Simultaneous quantitative determination of major phase I and II metabolites of ibuprofen in biological fluids by high-performance liquid chromatography on dynamically modified silica. *J. Chromatogr. B* **1997**, *696*, 235–241.
- [25] Tixier, C.; Singer, H.P.; Oellers, S.; Müller, S.R. Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen and naxoprofen in surface waters. *Environ. Sci. Technol.* **2003**, *37*, 1061–1068.
- [26] Zwiener, C.; Seeger, G.; Glauner, T.; Frimmel, F.H. Metabolites from the biodegradation of pharmaceutical residues of ibuprofen in biofilm reactors and batch experiments. *Anal. Bioanal. Chem.* **2002**, *372*, 569–575.
- [27] Dakiky, M.; Khamis, M.; Manasra, A.; Mereb, M. Selective adsorption of chromium (VI) in industrial waste water using low cost abundantly available adsorbents. *Adv. Environ. Res.* **2002**, *6*, 533–540.
- [28] Khamis, M.; Karaman, R.; Ayyash, F.; Qtait, A.; Deeb, O.; Manasra, A. Efficiency of advanced membrane wastewater treatment plant towards removal of aspirin, salicylic acid, paracetamol and p-aminophenol. *Journal of Environmental Science and Engineering* **2011**, *5*, 121–137.
- [29] Karaman, R.; Khamis, M.; Qurie, M.; Halabieh, R.; Makhazeh, I.; Mannasra, A.; Nir, S.; Nasser, A.; Bufo, S.A. Removal of diclofenac potassium from wastewater using clay-micelle complex. *Environ. Technol.* **2012**, *33* (11) 1279–1287.
- [30] Mishael, Y. G.; Undabeyita, T.; Rytwo, G.; Papahadjopoulos-Sternberg, B.; Rubin, B.; Nir, S. Sulfometuron adsorption via alkylammonium cations adsorption as monomers and micelles on montmorillonite. *J. Agri. Food Chem.* **2002**, *50*, 2856–2863.
- [31] Polubesova, T.; Zadaka, D.; Groisman, L.; Nir, S. Water remediation by micelle-clay system: Case study for tetracycline and sulfonamide antibiotics. *Water Res.* **2006**, *40*, 2369–2374.
- [32] Polubesova, T.; Nir, S.; Zadaka, D.; Rabinovitz, O.; Serban, C.; Groisman, L.; Rubin, B. Water purification of organic pollutants by optimized micelle-clay systems. *Environ. Sci. Technol.* **2005**, *39*, 2369–2384.
- [33] Zadaka, D.; Mishael, Y.G.; Polubesova, T.; Serban, C.; Nir, S. Modified silicates and porous glass as adsorbents for removal of organic pollutants from water and comparison activated carbons. *Appl. Clay Sci.* **2007**, *36*, 174–181.
- [34] Nir, S.; Zadaka-Amir, D.; Kartaginer, A.; Gonen, Y. Simulation of adsorption and flow of pollutants in a column filter: application to micelle-clay mixtures with sand. *Appl. Clay Sci.* **2012**, *67–68*, 134–140.