Removal of Two NSAIDs: Naproxen and Diclofenac and a Heavy Metal Cr (VI) by Advanced Membranes Technology.

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Abstract: *ODTMA-micelle-clay complex as an efficient adsorbent was prepared from a cationic surfactant, octadecyltrimethylammonium (ODTMA) and a negatively charged clay (montmorillonite). It is characterized with a positive charge and large hydrophobic sites. The micelle- clay complex was investigated towards removal of the ant-inflammatory drugs (NSAIDs), Diclofenac and Naproxen and a heavy metal Cr (VI) as part of comprehensive evaluation study to utilize this adsorbent in advanced wastewater treatment technology.*

Stability studies demonstrated that while Diclofenac potassium was completely stable in fresh water and in sludge Naproxen underwent biodegradation in sludge to provide O-desmethyl naproxen (DMN) as its single metabolite.

Al-Quds Wastewater Treatment Plant (WWTP) which includes ultrafiltration (UF) (hollow fiber HF and spiral wound SW) membranes, activated carbon (AC) and reverse osmosis (RO) has demonstrated high removal efficiency toward these two NSAIDs and Naproxen metabolite (DMN). Furthermore, the filtration results by Al-Quds WWTP revealed that the UF-HF membrane was not efficient in removing the three studied pollutants from wastewater. In contrast, the RO and AC membranes were found to be quite efficient in removing (100%) all studied pharmaceuticals.

The column filtration experiments with a mixture of sand and ODTMA-micelle-clay complex as adsorbent indicated 100% removal of the adsorbates, Diclofenac and Naproxen and Naproxen metabolite (SMN). Similarly, ODTMA-micelle-clay complex was found to completely remove the heavy metal Cr (VI) from its aqueous solutions at ambient pH and temperature.

Keywords: *wastewater treatment, ODTMA-micelle clay complex, Naproxen, Non-steroidal anti-inflammatory drugs, Cr(VI), Diclofenac, Activated carbon.*

1. Introduction

1.1. Pharmaceuticals and heavy metals in the Palestinian environment.

It is believed that the water sources in Palestine are contaminated with a variety of pollutants due to the absence of wastewater separation and limitation of sanitation sewer systems. Presently, raw or partially treated wastewater in many areas in Palestine is discharged through septic tanks, cesspits or flow free in open wades. Only a limited percentage of wastewater discharges to wastewater treatment plants.

The fates of all pollutants from untreated or partial treated wastewater are soil, surface or ground water. The pollutants which include pharmaceutical compounds, personal care products, heavy metals, fertilizers, oil, grease and pesticides are discharged from different applications in the Palestinian life.

1.2. Pollutants selected for the study

The pollutants selected for the current study were Diclofenac potassium, Naproxen sodium as pharmaceuticals and Chromium (VI) as an industrial contaminant, because all the mentioned pollutants are suspected to be present in the Palestinian environment due to their human and industrial uses.

1.2.1. The chemical structures of Diclofenac potassium and Naproxen sodium

Diclofenac potassium and Naproxen sodium are considered among the most non-steroidal anti-inflammatory drugs (NSAID). Their chemical structures are illustrated in Figure 1 (Appendix A) and their IUPAC names and physical and chemical characteristics are summarized in Table 1 (Appendix B).

1.2.2. Chromium (VI) as an industrial pollutant

Chromium (VI), known as hexavalent chromium, is the second most stable state of Cr. It is found in nature in different minerals (e. crocoite ($PbCrO4$) [1]. It is considered as an industrial contaminant in both soil and ground water, in addition of being a well-known carcinogen [2]. Chromium (VI) is discharged into environment from different industrial factories [3]-[4] and is considered as the most toxic form of Cr [5]-[6].

Adsorption on solid surfaces such as those of activated carbon and clay is a widely used method for removing organic contaminants from water and wastewater due to the high specific and surface properties of the adsorbent (solid). Kyriakopoulos G. et al. (2006) [7] have showed that active carbon is very efficient in removing pesticides from wastewater while Cruz-Guzman M. et al. (2005) [8] reported that one of the disadvantages of using activated carbon for the removal of different pollutants is the high cost process needed upon the regeneration of the adsorbent.

It is expected that modification of clay by incorporating an organic cations in the former inner layer such as in the case of ODTMA-micelle-clay complex will increase the adsorbent effectiveness for the removal of various types of pollutants. The chemical structure of the cationic surfactant ODTMA (octadecyltrimethylammonium) is shown in Figure 2 (Appendix A). The modified clay which contains ODTMA in micelles is capable of removing anions and neutral organic compounds when its critical micelle concentration (CMC) value is 0.3 mM. This complex by virtue of its positive charge with hydrophobic region is capable of binding negatively charged organic molecules and bacteria as well [9]-[19].

1.3. Statement of Art

The water shortage in the Mediterranean region is considered as very important and crucial issue for the majority of the population. Wastewater treatment can provide an excellent alternative to close the gap between the water demand and supply and to achieve all environmental protection purposes; in fact the use of an efficient and economic technology allows minimizing the risk related to the use of untreated wastewater.

1.4. Study Objectives

The micelle-clay complex filters are a promising system which can efficiently remove different contaminants. The micelle-clay complex is obtained by reacting montmorillonite and octadecyltrimethylammonium (ODTMA) bromide. This complex is characterized by a large surface area, positively charged and has hydrophobic sites. Several studies on this complex have shown it to be particularly useful in water purification.

The major aim of this research is to evaluate and explore the possibility of using ODTMA-micelle- clay complex in removing various pollutants of different nature from wastewater. This research compromises an important part of comprehensive study whose aims are to assess and evaluate the integration of micelle-clay complex within advanced wastewater treatment plants. The advance treatment systems may include activated sludge process, ultra-filtration membranes (hollow fiber and spiral wound membranes), activated carbon adsorbent and reverse osmosis among other components as needed.

The investigated pollutants are Diclofenac potassium and Naproxen sodium as pharmaceutical compounds and Chromium as industrial pollutant.

The wastewater treatment plant located at Al-Quds University campus in Abu-Dies is made from such integrations and samples will be taken for analysis from the different compartments of the plant.

The specific goals of this research were:

- Comparison between the efficiency of ODTMA-micelle- clay complex and activated carbon for the removal of different pollutants.
- Assessing the removal efficiency of advanced membrane technology in Al-Quds University wastewater treatment plant towards removal of different pollutants.

Figure 3 (Appendix A) summarizes the steps undertaken upon the removal of the previously mentioned pollutants from wastewater.

2. Experimental

2.1 Materials and Equipment

2.1.1 Chemicals

All chemicals were of analytical grade. The clay used was Wyoming Na- montmorillonite SWY-2 clay; obtained from the Source Clays Registry (Clay Mineral Society, Colombia, MO, USA). Quartz sand (grain size 0.8—1.2 mm) was obtained from Negev industrial minerals (Israel). Octadecyltrimethylammonium (ODTMA) bromide was obtained from Sigma Aldrich. potassium dichromate ($K_2Cr_2O_7$, Sigma, USA). Silver sulfate (Ag_2SO_4, Sigma, USA). Mercury (II) sulfate (HgSO4, Riedel-de Haen, Germany). De-ionized water was used to prepare all solutions. Microbiology growth media were obtained from Difco, USA (for total plate count, total coliform, and fecal coliform count, respectively). Pure Naproxen sodium was obtained as a gift from Beit Jalah (Palestine), Desmethyl Naproxen (DMN) was obtained from Sigma (Sigma Chemical Company, USA), Diclofenac potassium was obtained as a gift from Beit Jalah Pharmaceutical Company (Palestine) with 99% purity, Fine powder activated charcoal (FAC) with particle size ≤ 60.0 μm, and granular activated charcoal (GAC) with particle size ≤ 700.0 μm were obtained from Sigma (Sigma Chemical Company, USA). The powder was used for batch adsorption experiments while the granules were used in column experiments. Magnesium sulfate, methanol, acetonitrile, tetrahydrofuran (THF), and purified water were obtained from Sigma (USA). All solvents used were HPLC grade. High purity diethyl ether (>99%) was purchased from Biolab (Israel), orthophosphoric acid was obtained from Riedel-De Haen (Germany)

2.1.2 Instrumentations.

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 used was a Waters Alliance 2695 HPLC, equipped with a photodiode array detector (Waters Micromass® Masslynx™).Data acquisition and control were carried out using Empower™ software (Waters, Israel). Analytes were separated on a 4.6 150 mm C18 XBridge® column (5mm particle size) used in conjunction with a 4.6 20 mm XBridge™ C18 guard column. Microfilters 0.45mm (Acrodisc® GHP, Waters) were employed. The optimal conditions found for the analysis of naproxen were: mobile phase 20:80 (v/v) mixture of water/acetonitrile (pH adjusted to 3.45 using dilute o-phosphoric acid), flow rate 1.0 mL min^{-1}, UV detection at a wavelength of 240 nm.

Cr (VI) Solution pH was measured using pH-EC-TDS meter, HI 9812, Hanna instruments. Total chromium concentration was determined by Atomic Absorption Spectrometry (AAS) (AA-6200 Shimadzu). It is worth noting that this method gives total-Cr in solution, irrespective of the oxidation state of the metal. Cr(VI) was determined by UV-vis spectrophotometer (UV-1601 Shimadzu) using the diphenylcarbazide method.

The advanced wastewater treatment plant employed in this study is located at Al-Quds University-Palestine the effluent from this plant is recycled for the irrigation of plants cropped in the field of university Campus.

2.2 Methods

2.2.1 Efficiency of Al-Quds WWTP for the removal of Naproxen and Diclofenac potassium.

The efficiency of different treatment units was ascertained by spiking separately the secondary effluent with 31.0 mg L^{-1} of Naproxen and 31.15 mg L^{-1} of Diclofenac potassium. Samples were collected from different locations of the WWTP as depicted in Figure 4 (Appendix A). Before the analysis of Naproxen and Diclofenac potassium, SPE-C18 disposable cartridges were used to pre-concentrate 10 mL of each sample by adsorption of analytes. Recovery tests were performed using triplicate solutions of all substances, and values ranging from 98% to 102% were obtained.

2.2.2 Stability of Naproxen and Diclofenac potassium.

Stability studies of naproxen were performed at 25°C by dissolving 100 mg of Naproxen sodium or Diclofenac potassium either in 1 L of pure water or in 1 L of activated sludge samples from the wastewater treatment plant (WWTP) located in the Al-Quds University (Abu-Dies Main Campus, Palestine. Activated sludge was maintained under continuous aeration to permit the survival of microorganisms. Samples were collected time by time, filtered using 0.45-mm cellulose nitrate filters, stored at 4°C and analyzed by HPLC at the time. The degradation by-product, DMN, was extracted using solid phase extraction and lyophilized to have solid sample for batch experiment.

2.2.3 ODTMA-micelle-clay complex preparation.

The ODMTA micelle-clay complex was prepared by mixing a smectitic clay- mineral (montmorillonite) with the cationic surfactant octadecyltrimethylammonium (as bromide salt) with a critical micelle concentration (CMC) value of 0.3 mM as described previously [9]-[11]. The obtained complex by virtue of its positive charge and hydrophobic region is capable of efficiently binding neutral and negatively charged organic molecules [9]-[11].

2.2.4 Batch adsorption experiments.

Batch adsorption experiments were carried out on Naproxen, Diclofenac and Cr(VI) at different concentrations. Experiments were performed in 250 mL Erlenmeyer flasks containing 500 mg of either micelle-clay complex or granular activated charcoal; 100 mL of each drug solutions having known initial concentration were then introduced into each flask. The flasks were shaken in an electronic shaker for two to three hours at room temperature, and then the content of each flask was centrifuged for 5 min and filtered using 0.45 μm filters. The equilibrium concentrations of the contaminates were then obtained by HPLC for Naproxen and Diclofenac potassium whereas the total Cr measured using Atomic Absorption (AA) and Cr(VI) using UV/Vis method. To evaluate the effect of hydrogen ionic concentration on the adsorption reaction, the pH of a series of 50 mg L^{-1} Cr(VI) solutions was adjusted to the desired value in the range from 1 to 8, using either 1 M NaOH or 1 M HCl, and the adsorption process.

Equilibrium relationships between adsorbent and adsorbate were obtained by using Langmuir and/ or Freundlich adsorption isotherms. The linear form of the Langmuir adsorption isotherm was adopted according to Eq. (1):

$$Ce / Qe = 1/ (k\,Qmax) + Ce \qquad (1)$$

Where Ce is the equilibrium concentration of the pollutant in mg L^{-1}

Qe is the equilibrium mass of adsorbed pollutant per gram of complex or charcoal,

K is the Langmuir binding constant (L mg1), and

Qmax is the maximum mass of pollutant removed per gram of complex.

Freundlich isotherm describes the adsorption equilibrium on heterogeneous surface and its linear form is given by Eq. (2):

$$\text{Log } qe = \text{Log } k + 1/n\,(\text{Log } Ce). \qquad (2)$$

Where Ce is the equilibrium concentration of solute in mg L^{-1}

qe is the amount of solute adsorbed per unit weight of adsorbent, k is the relative adsorption capacity of the adsorbent and n is the intensity of the adsorption.

2.2.5 Column filtration experiments.

Column filtering experiments were performed using 50/1 (w/w) mixtures of quartz sand and either ODTMA-clay complex, or granular activated charcoal, 20 cm layered in borosilicate columns of 25 cm length and 5 cm diameter. Each column contained 13 g of complex, or GAC. The bottom of the column was covered with 3 cm layer of quartz sand. Quartz sand was thoroughly washed by distilled water and dried at 105 °C for 24h before its use. Solutions in pure water (1 L each) containing different Naproxen sodium, Diclofenac potassium and Cr(VI) concentrations (0.01, 1, 10, and 100 mg L^{-1}) were passed through either micelle-clay or granular activated carbon columns (one column for each solution). In all cases the flow rate was 2.0 mL min^{-1}. Eluted fractions were collected in all column experiments and analyzed. All experiments performed in three replicates and average values and standard deviations were calculated.

3. Results and Discussion

3.1 Performance of ODTMA-micelle-clay complex for removing pollutants and bacteria from tertiary treated wastewater.

This study is the first stage in a comprehensive evaluation of how the micelle-clay complex can be incorporated in a multi-stage procedure of wastewater treatments.

The efficiency of filters is based on the use of a micelle- clay complex to polish the tertiary treated wastewater that is generated from ultra-filtration plants by using hollow fiber membranes with 100 kD cutoff filters. Solutions of UF-hollow fiber permeate were passed through the column filter performed with 100/1, or 50/1 (w/w) mixtures of quartz sand and ODTMA-clay complex with two flow rate modes at 1.2 ml min^{-1}, and 50 ml min^{-1}.

COD, BOD, TSS, EC, turbidity and microbial counts (FC and TC) were measured for the initial solutions and in each collected fraction of 100 ml in low flow rate (1.2 ml min^{-1}). While in the second flow rate the samples were collected and measured after 1, 4, 9, and 14 liters.

Each measurement was repeated three times and their average and standard deviations were evaluated.

3.1.1 Results of low flow rate filtration (1.2 ml min^{-1})

Results of total suspended solids (TSS), turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), total bacteria count as total coliforms (TC) and fecal coliforms (FC) for all collected fractions (100 ml for each sample) showed a very significant reduction for all measured samples.

Results showed a reduction of TSS in (mg.l^{-1}) and of turbidity in (NTU) of collected samples from initial concentration of 6 mg.l^{-1} and 14 NTU respectively to zero value for both tests. On the other hand, the EC in (µS/cm) values were decreased to <950 µS/cm.

Pathogenic indicators FC and TC in (cfu) for all filtered samples showed a decrease of up to zero. The COD and BOD results summarized in Figure 5 (Appendix A) show dramatic reduction in both parameters.

The summary of low flow rate (1.2 ml min^{-1}) indicates that filtration of tertiary treated water obtained from HF ultra-filtration by micelle-clay complex with excess sand reduced significantly the FC, TC, BOD, EC, turbidity and COD of effluent.

3.1.2. Results of intermediate flow rate (50 ml min^{-1}) mode

In this experiment we employed a duplicate system, each consisting of two filters in series. The filters included a micelle-clay complex mixed with excess sand (1:100, w/w). The flow rate was 50 ml min^{-1}; the samples were collected after 1, 4, 9 and 14 liters from both columns. The initial values of TSS, turbidity, COD and BOD was 7 mg l^{-1}, 14 NTU, 80 mg l^{-1} and 53 mg l^{-1}, respectively. The results of TSS showed complete removal during the second column while in the first column no efficiency was observed after eluting 9 liters. The turbidity reduction was successful in the first column when eluting 4 liters but no reduction in turbidity was observed on the other fractions, 9 and 14 liters. On the other hand, the second column showed an efficient removal during the first 9 liters elution, however, little or no efficiency was observed when eluting up to 14 liters.

The results of COD and BOD in mg l^{-1} were reduced dramatically in both columns. The final BOD concentration after 14 liters elution in the first column was 12.5 mg l^{-1} and 13 mg l^{-1} in the second column. On the other hand, the final COD concentration after eluting up to 14 liters in both columns was 25 mg l^{-1} and 20.5 mg l^{-1} for the first and second columns, respectively.

The results in Table 2 (Appendix B) demonstrate that filtration by the micelle-clay complex reduced dramatically the number of pathogenic bacteria, fecal coliforms (FC) from an initial value of 50,000 cfu/100 ml to zero in the water emerging from the second filter after 14 liters, whereas for the first filter the corresponding number was 4. It should be noted that this reduction of pathogenic bacteria is without any disinfection. The total coliforms (TC) was reduced from initial value 70,000 cfu/100ml to zero after passage of 1liter and this number was increased to 5 after eluting 14 liters. In the second column the TC was reduced to zero after eluting 14 liters.

3.2 Removal of diclofenac potassium from wastewater using ODTMA-micelle-clay complex.

Diclofenac (2-[(2,6-dichlorophenyl)amino] benzene acetic acid) is one of the most commonly used non-steroidal anti-inflammatory drugs (NSAID); it is used to reduce inflammation, and as analgesic; reduces pain in disease conditions such as arthritis and acute injury.

The presence of an ionizable carboxyl group is emphasized in a much higher mobility of Diclofenac than as indicated by its log P (octanol–water distribution coefficient), and by a low sorption properties under the conditions of slow sand filtration or subsoil passage.

This study demonstrates an efficient method for the removal of diclofenac from water by using a composite micelle (octadecyltrimethylammonium (ODTMA)–clay (montmorillonite) positively charged, that has a large surface area and includes large hydrophobic domains.

3.2.1. Diclofenac stability test

The stability in pure water and in sludge was studied by adding 100 mg l^{-1} of Diclofenac in 1000 ml of water or sludge in Erlenmeyer flask. The monitoring results of Diclofenac potassium solutions at ambient temperature in both water and sludge for 30 days indicated that this substance is resilient to hydrolysis and to bacterial degradation.

3.2.2. The effect of time

3.2.2.1. Effect of initial concentration

Results of percentage removal of different initial concentrations of Diclofenac potassium by using charcoal and micelle clay complex showed a decreasing in the removal efficiency by increasing the initial concentrations for both adsorbents. The percentage removal of 200 mg l^{-1} of Diclofenac potassium was 98.5±0.1 and 100±0.1 for micelle-clay complex and charcoal, respectively, while the efficiency for 1000 mg l-^{1} decreased to 73.43±0.1 and 78.6±0.1 for the same adsorbents, respectively.

3.2.3. Adsorption isotherms

Batch adsorption experiments were carried out using solutions of Diclofenac potassium in the concentration range of 50-1000 mg l^{-1}. Experiments were performed in

250 ml Erlenmeyer flasks containing 0.5 g of either micelle-clay complex or charcoal: initial and final concentrations were measured to study the adsorption isotherm using Langmuir model. The linear relationship between Ce/Qe and Ce indicates that the adsorption of diclofenac potassium by the micelle-clay complex and charcoal fits Langmuir isotherm. The Q_{max} and k values were determined from the slope and intercept of the linear equation. These values for the clay-micelle complex were 153.8 mg g^{-1} and 0.07 l mg^{-1}, respectively, whereas the values for charcoal were 158.7 mg.g^{-1} and 1.2x10-3 l mg^{-1}, respectively. The Q_{max} for charcoal was higher than that for the micelle clay complex but the affinity coefficient, k, for the micelle-clay complex was 58 folds larger than that for charcoal.

3.2.4. Filtration experiments

Column filter experiments were performed by using 100/1, or 50/1 (w/w) mixtures of quartz sand and ODTMA- or BDMHA - clay complex (20 cm layer) in a column of 25 cm length and of 5 cm diameter. For a 100/1, or 50:1 ratios the active component layer in the filter included either 6.5 or 13 g of a complex, corresponding to 2 g or 4 g of ODTMA or BDMHA cations. The flow rate was varied between 2.0 ml min^{-1} to 60 ml min^{-1}. Fractions were collected for the assay of Diclofenac potassium content.

3.2.5. Effect of flow rate

The column filter which contained 13 g micelle clay complex (4.0g of ODTMA) was tested for the removal of 1000 ml of 1000 ppm Diclofenac potassium solution by collecting fractions (50 ml each fraction) with low flow rate (2 ml min^{-1}). The filtration results indicated a completed removal of Diclofenac potassium during an elution of 1000 ml containing 1000 mg l^{-1} of Diclofenac potassium.
Other experiments to investigate the high flow rate and the low concentration in ppb range were performed by using two systems, each consisting of two column filters in series. Each column contained a mixture of 650 g sand, 6.5 g of the micelle-clay complex, or 2 g of ODTMA with excess sand. The flow rate range was between 30-60 ml min^{-1}, while the concentrations variation was between 8-118 ppb. The results summarized in Table 3 (Appendix B) demonstrated a high efficiency of the filter in removing Diclofenac potassium.

3.2.6. Breakthrough curves: comparison between ODTMA-micelle-clay complex and activated carbon

The results listed in Figure 6 (Appendix A) demonstrated 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 which contained a mixture of 650 g sand with 6.5 g of micelle-clay complex, or 2.0 g of ODTMA. Up to 1.5 liters elution, this filter yielded a complete removal of Diclofenac potassium, and after 3 liters the percentage removal was slightly dropped to 93%. The filter which contained BDMHDA complex has yielded a removal of 93% for the passage of less than 0.5 liter, whereas at 3 liters less than 10% of Diclofenac was removed. Furthermore, the removal of Diclofenac using BDMHA-clay complex was accompanied by the appearance of very turbid filtrates indicating a possible decomposition of the complex. For the activated carbon, filters the removal efficiency was poor due to low capability of such filters to remove anionic and certain neutral pollutants.

3.2.7. The efficiency of Al-Quds WWTP towards the removal of Diclofenac

The performance of different treatment units were studied by entering 31.15±0.01mg.l^{-1} of Diclofenac potassium as initial concentration to WWTP plant. Seven wastewater samples were collected from different locations of the WWTP at Al-Quds University. The concentration of permeate solution of UF-HF unit (first treatment unit) was 10.34±0.01mg.l^{-1} while the brine product was 20.63±0.01 mg.l^{-1}. In the second treatment using UF-SW unit, the permeate solution concentration was 3.75±0.01 mg.l^{-1} while the concentration of permeate solution was 8.54±0.01mg.l^{-1}. The product of activated charcoal adsorbent process was 0.19±0.01 mg.l^{-1} and a complete removal of Diclofenac potassium was observed in the final treatment unit, reverse osmosis (RO).

3.3. Stability and removal of naproxen and its degradation product using advanced membrane wastewater treatment plant and ODTMA-micelle-clay complex.

Naproxen, a non-steroidal anti-inflammatory drug (NSAID), commonly used for fever, inflammation and for different health problems, has been recently detected in sewage effluents, surface and ground water, and even in drinking water. The aim of this study was to study the stability of Naproxen in Al-Quds activated sludge and to test the performance of advance integrated membrane wastewater treatment plant in terms of Naproxen removal from spiking wastewater samples. In addition, Naproxen removal using filters that included micelle–clay complex and activated carbon, and Naproxen adsorption isotherms on both adsorbents were studied.

3.3.1. Naproxen stability in fresh water and sludge

Naproxen degradation in fresh water and activated sludge was studied using 100 mg l^{-1} of Naproxen solution. HPLC monitoring study for Naproxen showed no degradation in fresh water for more than 30 days at room temperature, while it underwent biodegradation in activated sludge within three days. Figure 7 (Appendix A) shows Naproxen biodegradation to its metabolite, O- desmethyl-naproxen (DMN).

3.3.2. The removal of Naproxen by advanced membrane technology (Al-Quds WWTP)

Wastewater spiking experiment were used to investigate the efficiency of advanced membrane technology which includes ultra-filtration (UF), activated charcoal (AC), and reverse osmosis (RO) membranes. 18 g of Naproxen was dissolved in water and poured into the Wastewater Treatment Plant (WWTP). The results showed that ultra-filtration was not sufficient for complete removal of the spiked Naproxen whereas the RO was quite efficient. The UF physical properties (20-100 kD) allow small molecules to pass through the semi-membrane while the impermeability of RO membrane prevents the passage of such small substances.

3.3.3. Column experiment
The filtration experiment was performed by using a laboratory column (18 x 4 cm) prepared by mixing 3.0 g of micelle-clay complex and 147 g sand. Elution rate was 2 ml min^{-1} and eluted volume used to investigate the removal efficiency of Naproxen was1000 ml. Figure 8 (Appendix A) shows the removal efficiency by the column experiment.

3.3.4. Adsorption isotherms study

Batch experiments using 100 ml of Naproxen solution and its degradation product, O-desmethyl-naproxen, DMN (in 50-200 $mg.l^{-1}$ concentration range) were introduced into 250 ml Erlenmeyer flasks containing 0.5 g of adsorbent (ODTMA-micelle-clay complex or charcoal). The adsorption isotherms of Naproxen on micelle-clay complex and activated charcoal showed high efficiency in removing both, the parent drug and its metabolite. Using ODTMA-micelle-clay complex as adsorbent, the kinetic of DMN was $1.34 \cdot 10^{-2}$ $s^{-1}l$ mg^{-1}: and the removal was completed in ten minutes.
The results of the equilibrium relationship between adsorbent and adsorbate using Langmuir and Freundlich equations showed that Langmuir equation fits better the experimental data.
The calculated Q_{max} values for ODTMA-micelle-clay complex and activated charcoal were 71.42 and 18.87 $mg.g^{-1}$, respectively. The micelle-clay complex showed higher adsorption capacity with removal efficiency of 90% in 50 minutes.

3.4. Removal of Cr (VI) from aqueous solution using ODTMA-micelle-clay complex.

Chromium is a naturally occurring element that exists in rocks, animals, plants, and soil. Chromium (VI) is a toxicant most often used as a pesticide. Cr(VI) is known to cause cancer in humans.
In this study, the effectiveness of ODTMA-micelle-clay complex for the removal of Cr(VI) anion from aqueous solutions has been investigated using either clay (montmorillonite) or micelle-clay complex. Batch experiments have showed the effects of contact time, adsorbent dosage and pH on the removal efficiency of Cr(VI) from aqueous solutions. Langmuir adsorption isotherm was applied for experimental data. Filtration experiments, using columns filled with micelle-clay complex mixed with sand, were performed to assess Cr(VI) removal efficiency under continuous flow at different pH values.

3.4.1. Removal of Cr(VI) by ODTMA-micelle-clay complex

The removal efficiency of Cr (VI) using pure clay was not efficient at pH higher than 2. While by using ODTMA-micelle clay complex, the adsorption efficiency was 98% at pH between 1.0 and 3.0. On the other hand, the removal efficiency of Cr (VI) at pH 6 was more than 80%. The variation in the removal efficiency is due to the ability of Cr (VI) to a rising anions with different charge density when exposed to different pH values and undergo transformation into diverse oxidation states.

3.4.2. Filtration Experiment

Column experiments were performed using glass columns (18 x 4 cm) prepared by mixing 3.0 g of ODTMA-micelle-clay complex and 147 g sand. The results are summarized in Figure 9 (Appendix A). The results indicate that complete removal of chromium was achieved at all studied pH values. However, at pH 1 and 2 the breakthrough point was greater than 1000 ml, whereas at pH 3, 4 and 6 the saturation point was significantly lower with a value of about 500 ml. These results are consistent with those obtained from batch experiments, indicating that the elution volume plays an important role during the adsorption process at pH values higher than 2. Column experiments showed complete removal of Cr(VI) with possible reduction to Cr(III) after the breakthrough points.

3.4.3. Adsorption Isotherms

The Langmuir constants Q_{max} and k were calculated from the slope and the intercept of equation 1 giving values of 9.61 mg g^{-1} and 0.136 l mg^{-1}, respectively. The adsorption capacity and percentage removal at pH= 6 by using micelle-clay complex was higher than that obtained using low cost adsorbents (25-57%). These results showed the possibility of using ODTMA-micelle-clay complex for the removal of Cr (VI) from water without any significant pH adjustment.

4. Summary and Conclusions

The stability of naproxen and diclofenac in pure water and sludge was monitored by HPLC and the results demonstrated that while diclofenac was completely stable in both media during 30 days at ambient temperature, naproxen underwent a fast biodegradation in sludge to yield desmethyl-naproxen (DMN) as a single degradation product.
The efficiency of the WWTP at Al-Quds University consisting of ultrafiltration (hollow fiber HF and spiral wound SW), activated carbon (AC) and reverse osmosis (RO) membranes was investigated towards the removal of two NSAIDs, Naproxen and Diclofenac, and a heavy metal Cr(VI). The results revealed that the removal efficiency of HF and SW membranes was not sufficient whereas a complete removal was achieved upon passing the pollutants solutions through the activated carbon and reverse osmoses (RO) membranes.
The removal of the two NSAIDs, naproxen metabolite (DMN) and Cr (VI) using ODTMA-micelle-clay complex was studied and compared with that of activated charcoal. The adsorption results revealed that ODTMA-micelle-clay complex was more efficient in removing these pollutants than activated carbon as judged by the calculated Q_{max} and k for both adsorbents.
The combined results suggest that incorporation of the ODTMA-micelle-clay complex into Al-Quds WWTP is promising and has the potential to be more efficient in removing anionic and neutral organic and inorganic pollutants.

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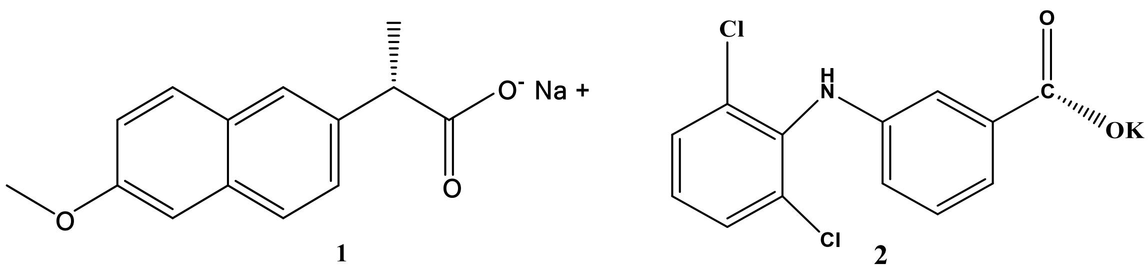
Appendix A



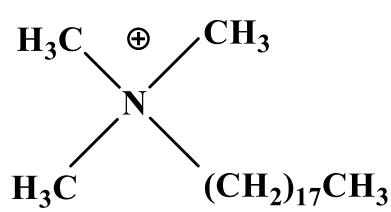
1

Naproxen Sodium

2

Diclofenac Potassium

Fig. 1 Chemical structures for Naproxen Sodium and Diclofenac Potassium



5

Octadecyltrimethylammonium (ODTMA)

Fig. 2 Chemical structure of octadecyltrimethylammonium (ODTMA).

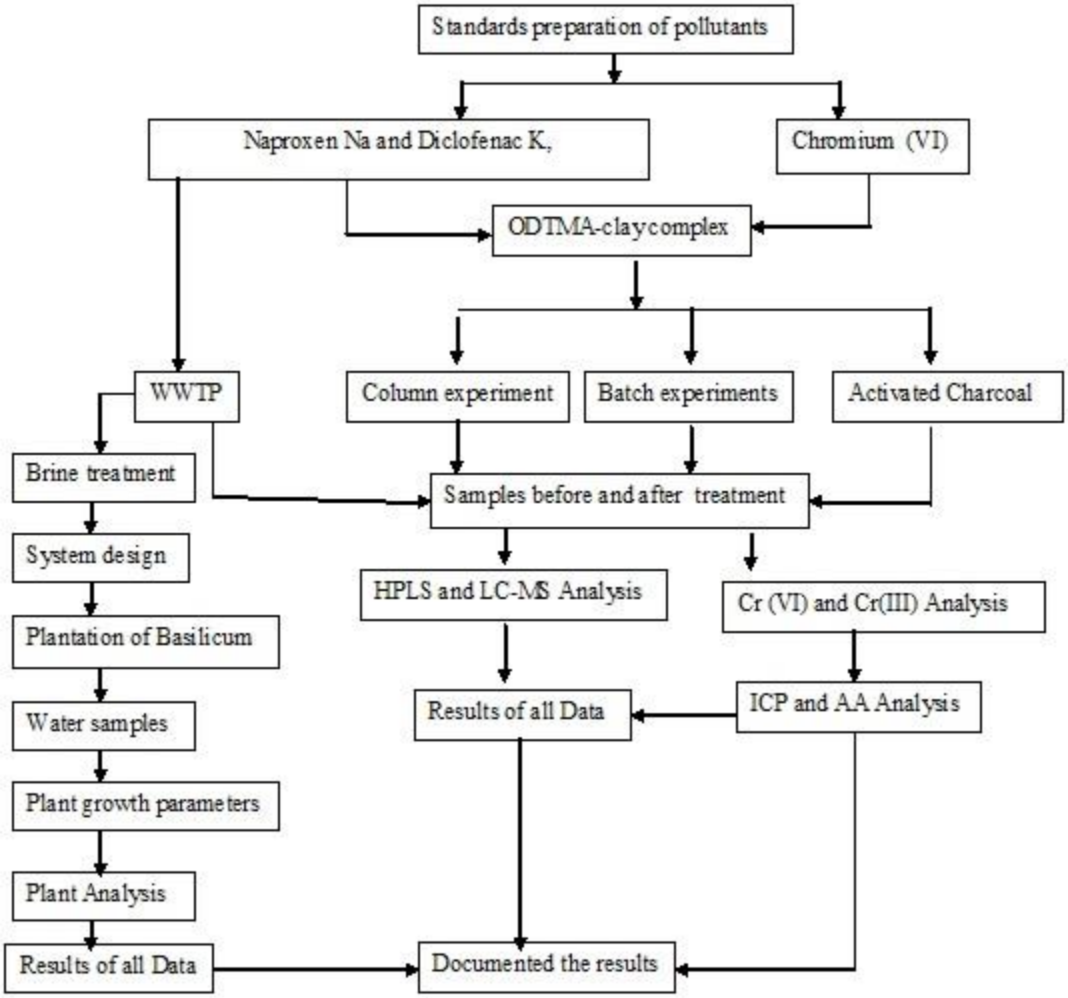


Fig. 3 Flow Chart for All Purification Pollutants Water Experiments.

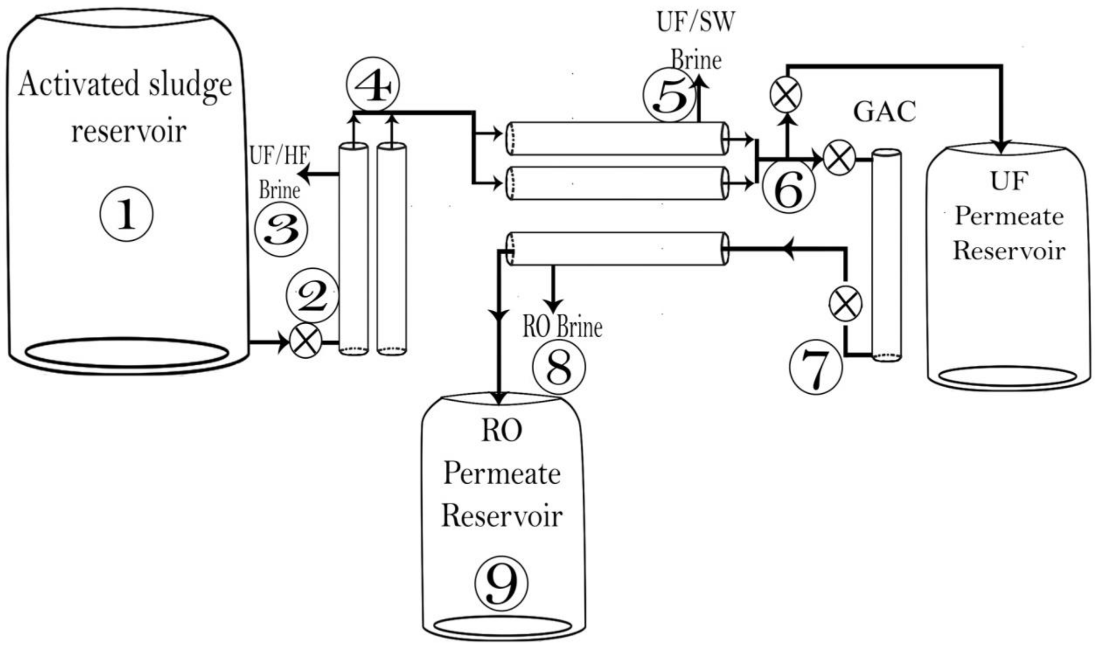


Fig. 4 Flow diagram schematizing the WWTP at Al-Quds University. Sampling sites are indicated by numbers. UF/HF, hollow fiber ultrafiltration membrane; UF/SW, spiral wound ultrafiltration membrane; RO, reverse osmosis; GAC, granular activated charcoal filter.

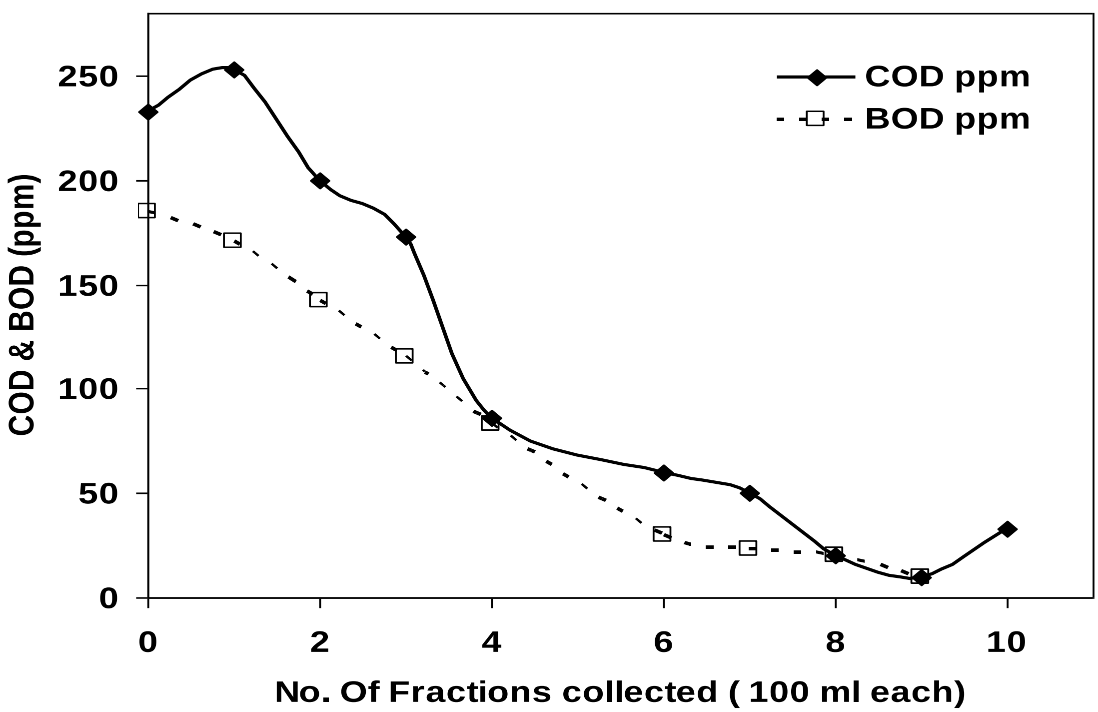


Fig. 5 Variation of the chemical oxygen demand (COD) and biological oxygen demand (BOD) in different fractions collected from micelle-clay sand column. The micelle-clay sand ratio was 1:50. The flow rate was 1.2 ml min^{-1} at room temperature. The volume of each fraction was 100 ml.

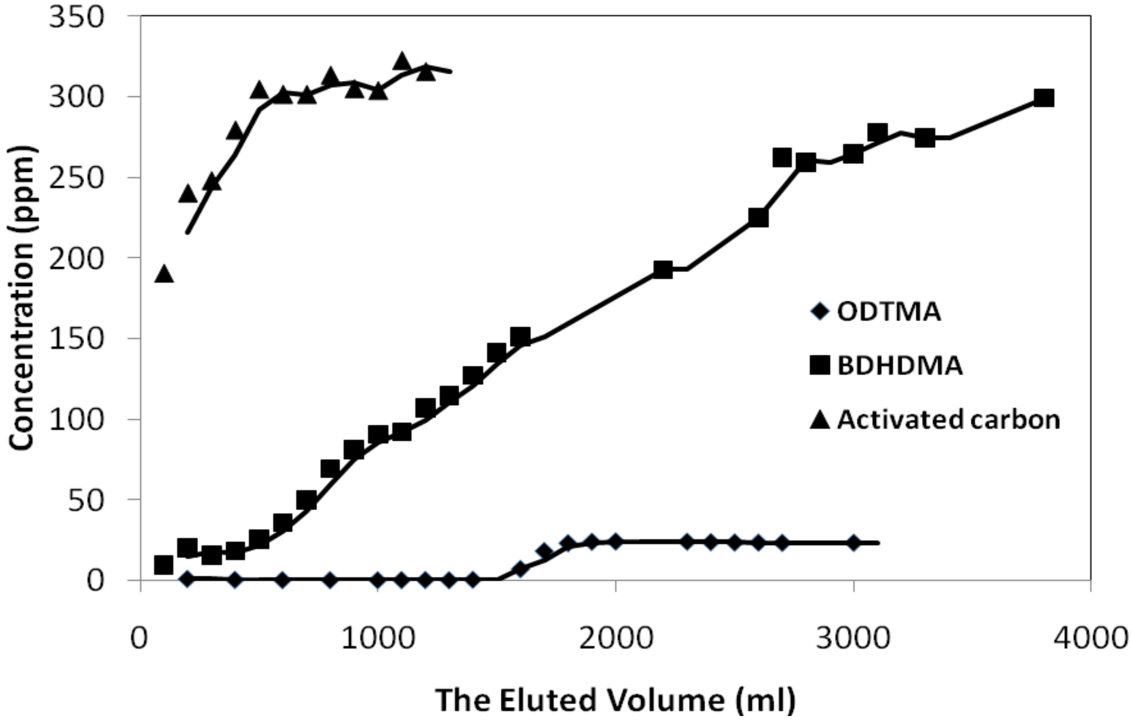
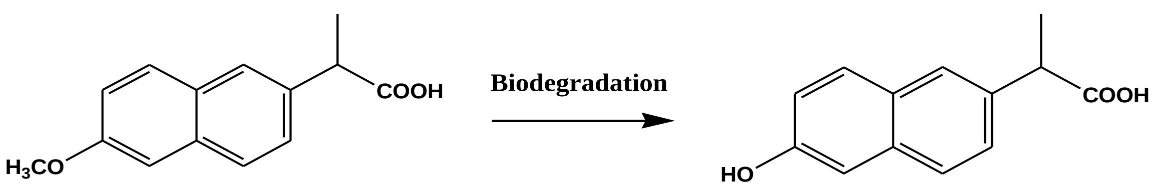


Fig. 6 Emerging concentrations of diclofenac from filters including activated carbon or micelle-clay complexes in which the organic cation was ODTMA or BDMHDA. The filters included excess sand (100/1 w/w). The weight of the active ingredient, i.e., ODTMA, BDMHDA or activated carbon was 2g in all cases, and filtration was at room temperature, at a flow rate of 20 ml.min^{-1} and the initial potassium diclofenac solution was at a concentration of 300 mg.l^{-1}.



Naproxen O-desmethyl-naproxen

Fig. 7 Biodegradation of naproxen to O-desmethyl-naproxen

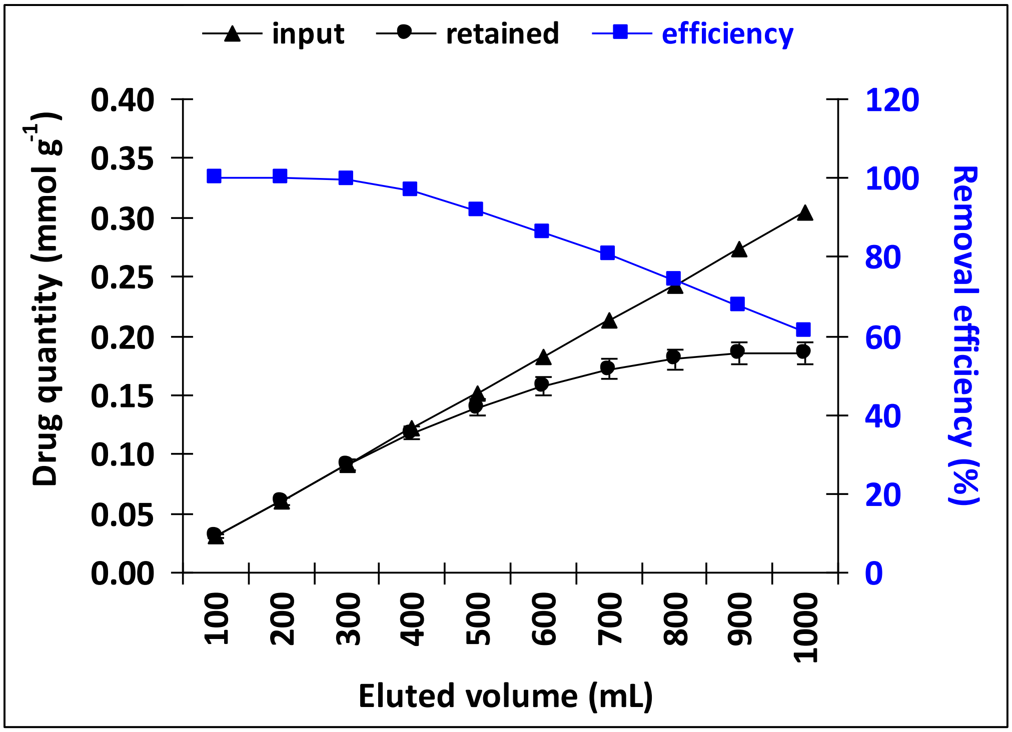


Fig. 8 Efficiency of filtration experiment

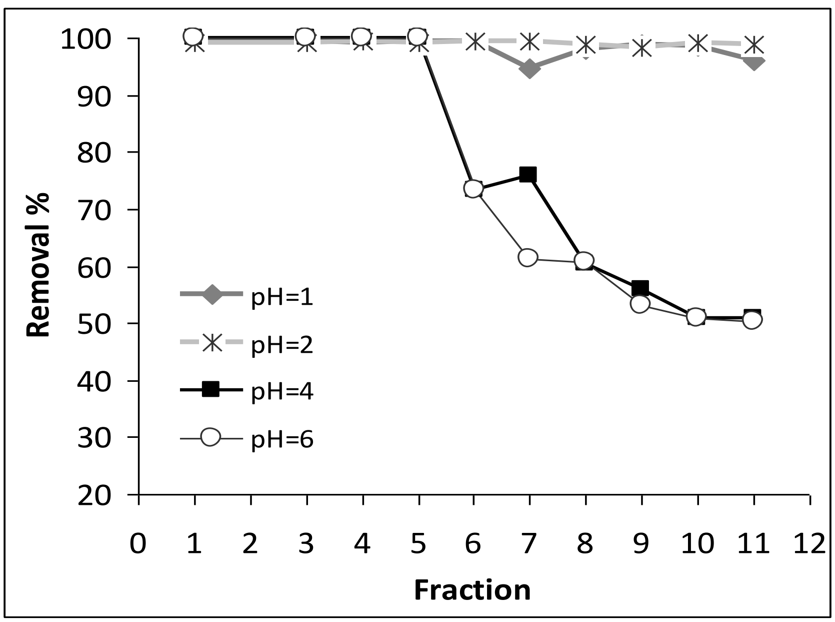


Fig. 9 Removal efficiency of Cr(VI) from solutions at different pH values by using column filtration on micelle-clay complex/sand system.

Appendix B

Table 1 The IUPAC name, chemical and physical properties of Diclofenac potassium and Naproxen Sodium.

Characteristic	Diclofenac potassium [20].	Naproxen Sodium [21].
IUPAC name	Benzene acetic acid, 2[(2,6-diclorophyenyl)amino] mono-potassium.	(S)- (+0-6 methoxy-α-methyl-2-naphthalene-acetic acid).
Molecular formula	$C_{14}H_{10}Cl_2KNNaO_2$	$C_{14}H_{13}O_2Na$
Molecular weight	334.24	252.24
Melting point (°C)	283-285	244-246
LD50 mg/kg	62.5	400
Solubility	Sparingly soluble in water, freely soluble in methanol, soluble in alcohol, slightly soluble in acetone,	soluble in water, soluble in methanol, sparingly soluble in alcohol, slightly soluble in acetone, practically insoluble in chloroform and Toluene

Table 2 Microbial removal (FC, TC, and TPC) in colony forming unit (cfu) per 100 ml of wastewater after filtration at a flow rate of 50 ml min^{-1} by two columns in series, which included micelle- clay complex mixed with excess sand (1:100, w/w)[a] .

Volume (L)	FC Per 100 Ml	TC Per 100 mL	TPC Per 100 mL
Inlet	50,000	70,000	300,000
1	0 (0)	0 (0)	1000 (2750)
9	0 (1)	1 (2)	2000 (22,000)
14	0 (4)	0 (5)	39,000 (70,700)

[a.] Values in parenthesis refer to first column. Results are average values from two systems in duplicate.

Table 3. Filtration of diclofenac potassium in the ppb range. Emerging concentrations of diclofenac from two filters in series including a micelle-clay complex in which the organic cation was ODTMA.

Initial conc. (ppb)	Flow rate (ml min^{-1})	Vol. (liter)	column 1		column 2	
			Diclofenac (ppb)	percent removed	Diclofenac (ppb)	percent removed
118	30	20	0	100	0	100
118	30	46	0	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				