REMOVAL FROM WASTEWATER OF PHARMACEUTICAL RESIDUES BELONGING NON-STEROIDAL ANTI-INFLAMMATORY DRUGS CLASSES USING ACTIVATED CARBON MATERIAL

Leon COVALIU[1], Florinela PIRVU[1],[2], Cristina Ileana COVALIU-MIERLĂ[1]

This article presents the study of anti-inflammatory drugs residues removal from wastewater using activated carbon material. For the adsorption and desorption studies were used four anti-inflammatory drugs: acetaminophen, diclofenac, ibuprofen and ketoprofen. The physical-chemical properties of the synthetic pollutants were studied varied the pH, the concentration and the contact time of the drug residues. To highlight the mathematical model which described very well the adsorption processes were used Langmuir and Freundlich isotherm. To demonstrate the presence of the drugs residues in wastewater were used total organic carbon (TOC) technique. Three concentrations of drugs were experienced: 1mg/L, 5mg/L and 10 mg/L and the amounts of activated carbon material used were 0.1g, 0,5g and 1g. The maximum efficiency of removing anti-inflammatory drugs residues from wastewater were recorded at pH=6, 1mg/L initial pollutants concentration and 1g adsorbent dosage. The removal efficiency for drug residues was as follows: acetaminophen (88%) > diclofenac (82%) > ketoprofen (79%) > ibuprofen (77%).

Keywords: activated carbon material, anti-inflammatory drug residues, wastewater

1. Introduction

The development of the production of a very large number of types of medicines has improved the quality of life of people and animals. On the other hand, pharmaceutical residues end up in the aquatic environment, and in the last decade it has become a major threat to the environment [1-2]. The possible ways for pharmaceutical products to enter the aquatic environment can be the following: the discharge of domestic, industrial wastewater, medicinal waste, aquaculture [2-4] which enter the environment in the form of the active substance of the medicine as well as their degradation products or as metabolites. The

[1] Prof., National University of Science and Technology, POLITEHNICA Bucharest, Romania, e-mail: cristina_covaliu@yahoo.com
[1] PhD student, National University of Science and Technology, POLITEHNICA Bucharest, Romania, e-mail: florinela_pirvu@yahoo.com,
[2] National Research and Development Institute for Industrial Ecology - ECOIND, Bucharest, Romania

quantities of medicinal products that enter the sewage treatment plants may differ depending on the physical and chemical properties of the medicine. Due to their hydrophobic properties and their stability, NSAIDs, (nonsteroidal anti-inflammatory drugs) can remains in the aqueous phase, therefore it can be found in surface waters at concentrations of up to ng/l [3-6]. Several methods have been applied to treat or eliminate NSAIDs from the aquatic environment.

Photocatalytic degradation [4-7]: The photocatalytic degradation was determined by sunlight of TiO_2. This was obtained through a process assisted by the ultrasound bath and their structural, photocatalytic and optical properties were characterized. Optimizing the photocatalytic degradation method involved experiments that were influenced by dose, pH, and initial drug concentration. The results of the photocatalytic experiments showed that there was a photodegradation of the solution of ketorolac tromethamine (NSAID) with a concentration of 10 mg/L of approximately 99%, with an optimized amount of TiO_2, 0.5 g/L and pH=4.4 in sunny conditions.

Biodegradation [5-9]: Laboratory tests were done with four NSAIDs (naproxen, ibuprofen, diclofenac and ketoprofen) in different aerobic, anaerobic, anoxic and sulfate-reducing conditions to evaluate the abiotic and biotic degradation of a surface water. The results of the experiment showed that the removal of the compounds decreases under conditions where the concentration of dissolved oxygen in the surface water decreases. After the study, all the compounds showed that they can be biodegradable under aerobic conditions, and their half-life of dissipation can be between 1.6 - 20.1 days. The dissipation half-lives for ketoprofen and naproxen increase by a correlation coefficient of 2 under the conditions tested in the absence of oxygen.

Biofiltration [10-13], COD (chemical oxygen demand): The study shows the possible use of the zebra mussel for removal of pharmaceutical contaminants that cannot be sufficiently removed from wastewater. Mollusks are resistant to anthropogenic and natural stress, have filtering capacity and could be used to bioaccumulate the lipophilic substances of contaminants. The data obtained demonstrated the ability of these mollusks to reduce the concentrations of some pharmaceutical products, suggesting a possible evaluation of the biofiltration process in wastewater management [11-12]. This flotation-electrocoagulation process was used to remove NSAIDs (diclofenac, ketoprofen and ibuprofen) from wastewater. Cetyltrimethylammonium ammonium bromide (CTAB), a cationic surfactant, was added as a foaming agent, and NSAID removal was significantly improved, over 45% in single NSAID wastewater systems.

For the removal of several NSAIDs pharmaceutical compounds, the concentration of CTAB used for good removal was equal to the sum of the molar concentrations of all NSAIDs. The removal of several NSAIDs from wastewater collected from hospitals was lower due to hydrophobic substances and oil interference found in the samples used, microextraction (3) and adsorption, HPLC-UV [11-12]. Adsorption mechanisms of naproxen (NAP), acetaminophen (ACT) and clofibric acid (CFA-active metabolite) on porous silica-based materials were exams. Advances in nanotechnology offer opportunities to treat wastewater much more efficiently and fast using affordable nanomaterials. Due to the characteristics of their surface and their unique structure, nanomaterials are suitable and effective adsorbents for removing drug residues from wastewater [11-12].

Adsorbents with mesoporous silica content compared to activated carbon in powder form, had a better adsorption capacity for CFA, on the other hand, activated carbon had a better adsorption capacity for ACT and NAP. The adsorption capacity of silica was higher at pH 5. The possible mechanisms were hydrogen bonds and electrostatic interactions. The adsorption capacity of hydrophilic adsorbents for acidic pharmaceuticals can vary due to their pKa values. Activated carbon (AC) is a carbonaceous solid with numerous micropores, large surface area and high adsorption capacity [13-15]. The successful application of activated carbon to the removal of pharmaceutical contaminants from wastewater depends on the properties of the activated carbon which may vary depending on the preparation technique and raw precursors used [16-20].

The purpose of the paper was to highlight the use of activated carbon material for the anti-inflammatory drug residues removal from a synthetic wastewater and also the detection technique for these organic pollutants. The drug products studied in this work were: acetaminophen (ACF), diclofenac (DCF), ibuprofen (IBF), ketoprofen (KET) which are part of the class of non-steroidal anti-inflammatory drugs (NSAIDs).

2. Experimental part

2.1. Materials and methods

The materials used in this study were purchased from Sigma-Aldrich. The purity of acetaminophen was ≥95.0%, ibuprofen ≥97.0%, ketoprofen ≥99.0% and diclofenac ≥99.0%. Solvents used for total organic carbon analysis (TOC) were purchased from Honeywell. Activated carbon material was purchased from Trace Elemental Instruments with a particle size between 10 and 50 µm. The carbon material has the following characteristics: specific surface area $604 m^2/g$, total pore volume $12,7 cm^3/g$ and average micropore radius 870Å.

2.2. Adsorption studies

Adsorption experiments were performed using synthetic wastewater having three different concentrations of anti-inflammatory drugs (1mg/L; 5mg/L and 10 mg/L), at two different pH values (4 and 6) using three different quantities of activated carbon material for the adsorption process (0,1g, 0,5g and 1g). All experiments were carried out in Erlenmeyer flasks (100mL) using a temperature controlled orbital shaker (stirring speed of 100 min^{-1}) for 120 minutes. The experiments were performed at room temperature (25±2^{0}C).

The removal efficiencies were calculated using the following equation (1):

$$\eta = \frac{C_i - C_f}{C_i} * 100 \quad (1)$$

where: C_i - the initial concentration of anti-inflammatory drugs (mg/L); C_f - the final concentration of anti-inflammatory drugs (mg/L).

2.3. Desorption studies

The desorption studies have been applied to highlight the drug residues retained on the adsorbent material and the possibility of using this material in other removal studies. The desorption procedure was as follows: samples of 1mg/L loaded with synthetic pollutants were stirred with 50 ml of HCl with different concentrations (0,1M; 0,3M and 0,5M) on a mechanical shaker (90 minutes at 150 rpm). The supernatant obtained was centrifugated and analyzed using the TOC technique.

The desorption of drug residues from activated carbon materials was calculated using the following equation (2):

$$\text{Desorption (\%)} = \frac{\text{Cd}}{(\text{Q} * \text{m})} * 100 \quad (2)$$

Where:
Cd is the concentration of drug residues desorbed from adsorbent material (mg/L);
Q is the adsorption capacity (mg/g);
m(g) is the mass of adsorbent material applied in experiment

2.4. Total Organic Carbon (TOC)

The pollutants residues from synthetic wastewater were monitored using TOC technique (total organic carbon). Another means for measuring the organic matters present in the wastewater is the TOC, which is especially applicable to small concentrations of organic matter. This TOC is performed by injecting a known quantity of sample into a high-temperature furnace or chemicallyoxidizing environment. The organic carbon is oxidized to carbon dioxide in the presence of a catalyst. The carbon dioxide that was produced was quantitatively measured by means of an infrared analyzer. Acidification and aeration of the sample prior to analysis eliminate errors due to the presence of inorganic carbon. The test can be performed rapidly and is becoming more popular.

The performance parameters of the TOC method are as follows: the detection limit (0.1mg/L), the quantification limit (0.3mg/L) and the extended uncertainty of the analysis method 12%. The name of the equipment used for the experiments is Shimadzu Analyzer TOC TN LCPN.

3. Results and discussion

3.1. Adsorption studies

The removal efficiency of drug residues (acetaminophen, diclofenac, ketoprofen and ibuprofen) from a synthetic wastewater was evaluated at two values of pH (4 and 6), three pollutants concentration (1mg/L, 5mg/l and 10mg/L) and three adsorbent dosages (0.1g; 0.5g and 1g). The main results are presented in Figs. 1a to 1d, and also in Fig. 2.

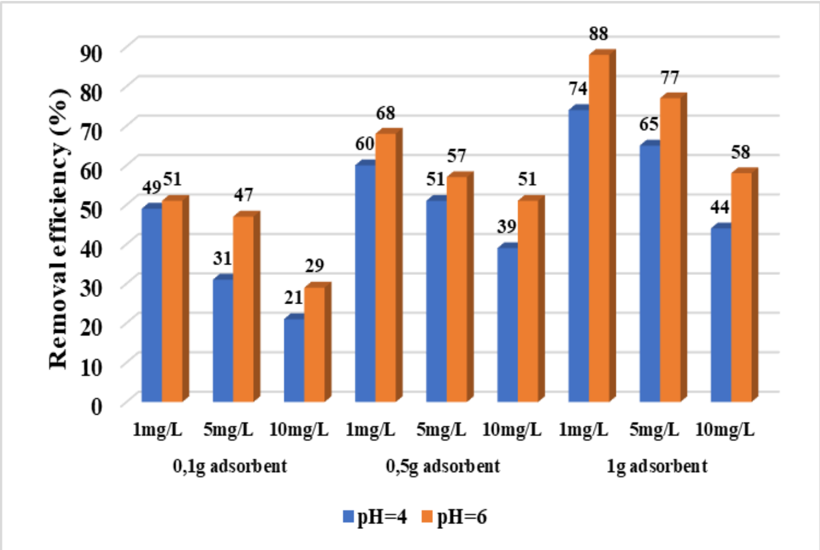

Fig. 1a. The effect of the pH on the acetaminophen drug residues removal at different concentration and adsorbent dosage

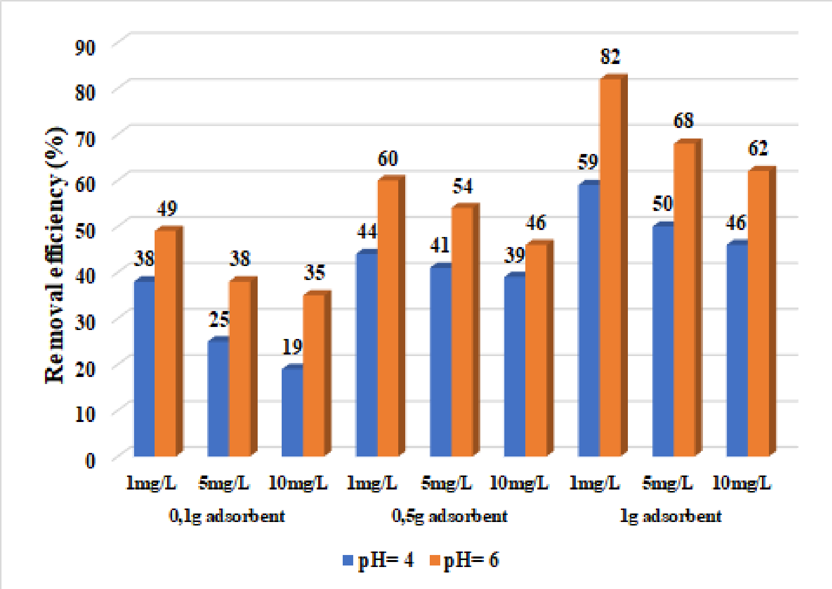

Fig. 1b. The effect of the pH on the diclofenac drug residues removal at different concentration and adsorbent dosage

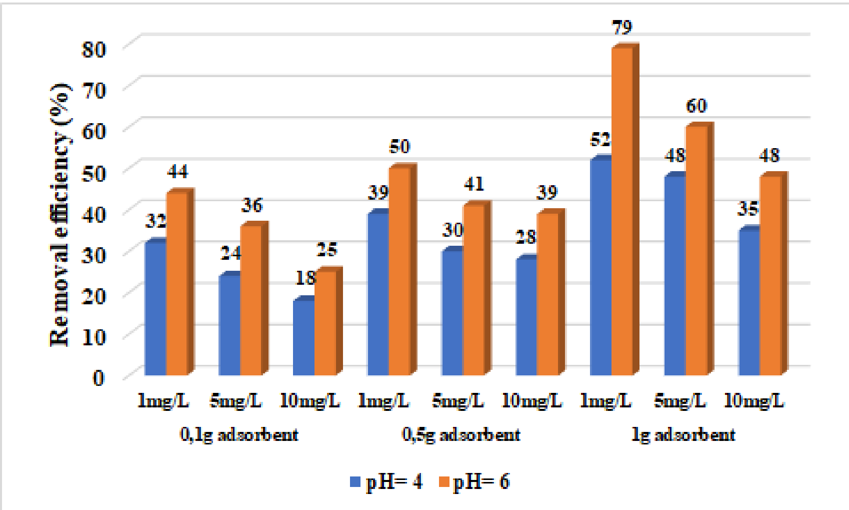

Fig. 1c. The effect of the pH on the ketoprofen drug residues removal at different concentration and adsorbent dosage

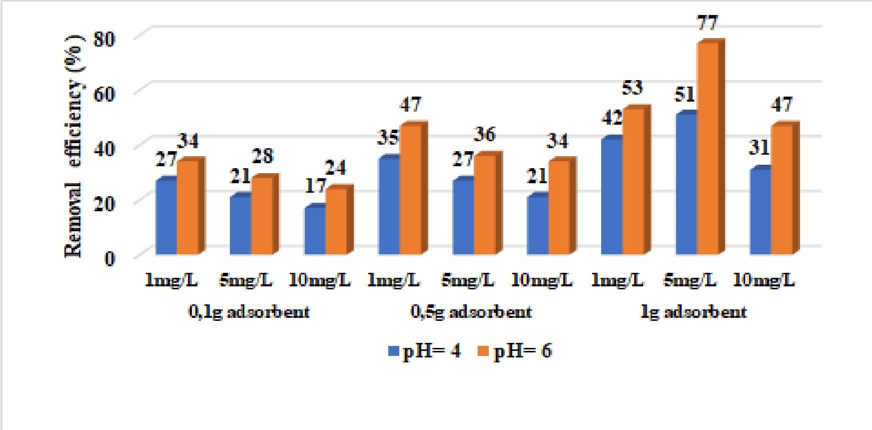

Fig. 1d. The effect of the pH on the ibuprofen drug residues removal at different concentration and adsorbent dosage

The adsorbent dosage is very important in adsorption studies. The activated carbon (adsorbent material) has a higher specific surface area (604m^2/g) which allowed all the adsorption processes on his sites. With 1g adsorbent material, at pH=6 was obtained the highest results for removal efficiency in comparison with 0.1g adsorbent material, also at pH=6, which presented the lowest removal efficiency as it is showed in Fig. 1a to 1d. The results obtained for the four drug residues are as follows with 1g adsorbent dosage, 1mg/L initial concentration and pH=6 (Fig. 1a to 1d): **acetaminophen (88%) > diclofenac (82%) > ketoprofen (79%) > ibuprofen (77%).**

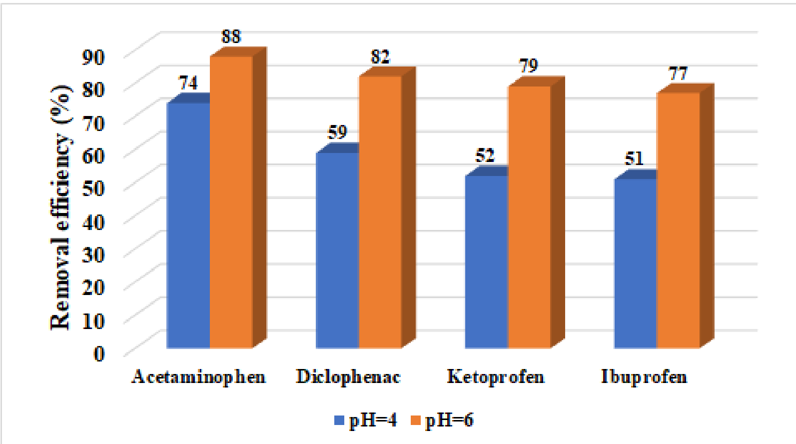

Fig. 2. The effect of the pH on the drugs residues removal at different pollutants concentration and adsorbent dosage

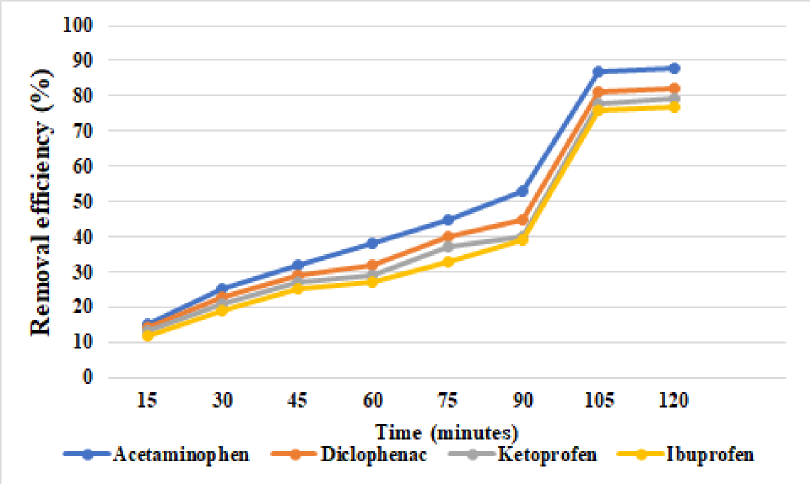

Fig. 3. Removal efficiency versus contact time

Fig. 2 showed the importance of the pH value of wastewater in the treatment process. In all cases, the treatment efficiencies were maximum. However, the pH value 6 is much more advantageous for removing drug residues from wastewater by observing the shorter treatment time (120 minutes).

These studies want to highlight the importance of TOC (total organic carbon) determination for a small concentration of the organic matter from wastewater. The effect of contact time on synthetic wastewater at pH 6 has been studied and the results are presented in Figs. 3. The removal efficiency of four drug residues presented high values at 6 value of pH, and low values at pH=4. After a contact time of 120 minutes, the adsorbent material becomes saturated and no longer adsorbs drug residues. The equivalence point is reached and the adsorption process ends.

3.2. Langmuir and Freundlich adsorption isotherms

To describe the best adsorption process are used the Langmuir and Freundlich mathematical models which are described elsewhere [16].

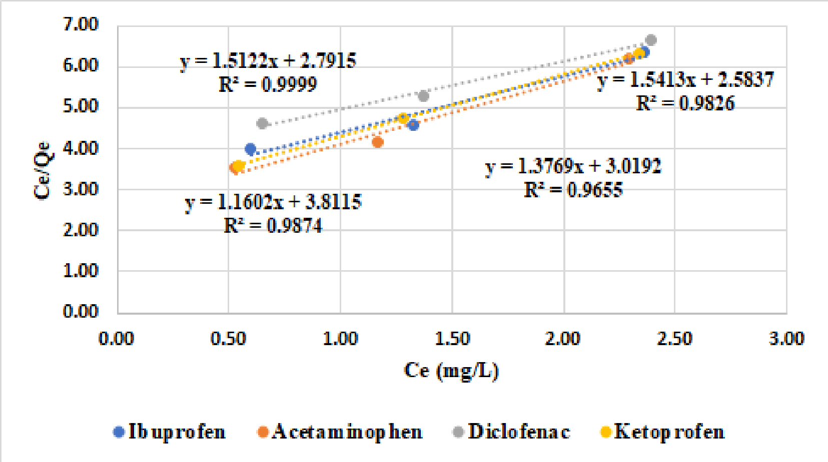

Fig. 4. Langmuir linearized isotherm for drug residues adsorbed onto activated carbon material

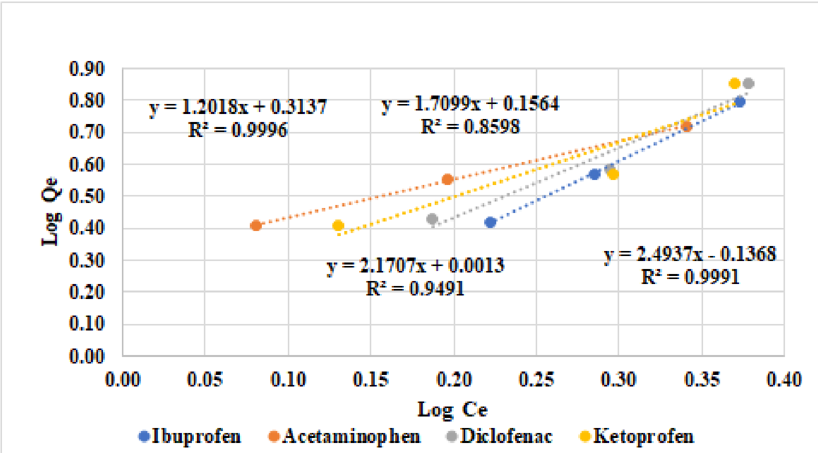

Fig. 5. The Freundlich isotherm for drug residues adsorbed onto activated carbon material

Table 1.

Langmuir and Freundlich adsorption parameters

	Langmuir parameters				**Freundlich parameters**		
Drug residues	Q_{max}(mg/g)	K_L (L/mg)	R_L	R^2	K_F (L/g)	1/n	R^2
Acetaminophen	0.64	1.62	0.28	0.9826	1.20	0.31	0.9996
Ibuprofen	0.70	2.70	0.10	0.9655	2.49	0.14	0.9991
Diclofenac	0.85	3.23	0.41	0.9874	1.55	0.21	0.9491
Ketoprofen	0.66	1.85	0.18	0.9999	1.71	0.16	0.8598

The experimental conditions for Langmuir and Freundlich isotherms are: initial pollutant concentration 1mg/L, pH=6 and 1g adsorbent dosage. Experimental data presented in Figs. 4 to 5, and Table 1 revealed that Langmuir isotherm model fits very well the experimental data for diclofenac (R^2=0.9874) and ketoprofen

(R^2=0.9999) and Freundlich models fits very well the data for acetaminophen (R^2=0.9996) and ibuprofen (R^2=0.9991) drug residues based on the correlation factor (R^2).

3.3. Desorption studies

The results for the desorption studies are presented below:

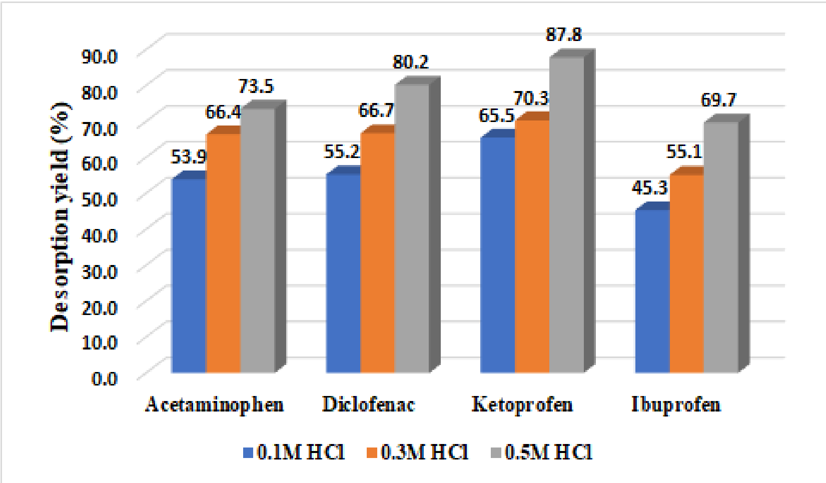

Fig. 5. The desorption studies

As it can be seen in Fig. 5, the ketoprofen residues (87.8%) are desorbed very well in the presence of 0,5M HCl solution, followed by diclofenac (80.2%), acetaminophen (73.5%) and ibuprofen residues (69.7%). All the experiments were performed using 1g of adsorbent material and 1mg/L synthetic pollutant solutions. The desorption duration was 90 minutes for all the pollutants tested in this study. All the experiments highlighted that adsorbent material used in this study can be re-used in other adsorption studies. Our activated carbon material is cheap and friendly with the environment.

4. Conclusions

This study wants to highlight the use of the TOC technique for wastewater at very low concentrations of organic pollutants, as well as the use of activated carbon as an adsorbent material for drug residues.

Anti-inflammatories such as paracetamol, diclofenac, ketoprofen and ibuprofen end up in city sewers and break down under certain environmental conditions. Their drug residues or by-products formed in wastewater must be monitored according to legislation in force.

Following the experiments presented in this article, it was found that the efficiency of removing drug residues from synthetic wastewater was maximum. In the case of synthetic wastewater with pH 6, using an amount of 1g of adsorbent material, the required treatment time was 120minutes for the initial concentrations of drug residues of 1mg/L. Two mathematical models were used to described the adsorption processes. Based on the correlation factor (R^2) it can be concluded that Langmuir model fits well the data for diclofenac and ketoprofen and Freundlich model fits well the data for acetaminophen and ibuprofen.

Since the organic pollutants in the synthetic wastewater is relatively fixed, the accuracy of the sample detection is ensured, with the TOC technique.

The results obtained also in this study indicate the feasibility of using activated carbon as adsorbent material for removal of drug residues from wastewater.

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