ECOTECHNOLOGY REMOVAL FROM WASTEWATER OF FOUR ANTI-INFLAMMATORY DRUGS USING ACTIVATED CARBON MATERIAL

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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 production of various types of medicines has significantly enhanced the well-being of both humans and animals. However, a downside to this progress is the contamination of aquatic ecosystems by pharmaceutical residues, which has emerged as a significant environmental threat over the past decade [1-2]. There are multiple pathways through which pharmaceutical products can find their way into aquatic environments, including the discharge of domestic and industrial wastewater, improper disposal of medicinal waste, and contamination from aquaculture activities [2-4]. These substances enter the environment in the form of the active ingredients of the medicines as well as their breakdown products or

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metabolites. The quantities of pharmaceuticals entering sewage treatment plants can vary based on the physical and chemical properties of the medication.

Photocatalytic Degradation [4-7]: This approach involves the degradation of NSAIDs, such as ketorolac tromethamine, using sunlight and titanium dioxide (TiO_2). Optimizing this process includes factors like dosage, pH, and initial drug concentration.

Results indicate that in sunny conditions, approximately 99% of the 10 mg/L ketorolac tromethamine solution can be photodegraded with an optimized TiO_2 amount of 0.5 g/L at pH 4.4.

Biodegradation [5-9]: Laboratory tests assessed the abiotic and biotic degradation of four NSAIDs (naproxen, ibuprofen, diclofenac, and ketoprofen) under different conditions (aerobic, anaerobic, anoxic, sulfate-reducing). The study revealed that the removal of these compounds is influenced by dissolved oxygen levels in surface water. Under aerobic conditions, all compounds demonstrated biodegradability with dissipation half-lives ranging from 1.6 to 20.1 days. Ketoprofen and naproxen exhibited extended half-lives under oxygen-depleted conditions.

Biofiltration [10-13], COD (Chemical Oxygen Demand): Zebra mussels were considered for the removal of pharmaceutical contaminants that are challenging to eliminate from wastewater. These mollusks, known for their resilience and filtration capabilities, showed promise in reducing pharmaceutical concentrations, suggesting their potential use in wastewater management. Additionally, a flotation-electrocoagulation process, enhanced with cetyltrimethylammonium ammonium bromide (CTAB), proved effective in removing NSAIDs (diclofenac, ketoprofen, and ibuprofen) from wastewater.

Adsorption [11-12]: The adsorption mechanisms of naproxen (NAP), acetaminophen (ACT), and clofibric acid (CFA-active metabolite) onto porous silica-based materials were investigated. Nanomaterials were explored for their efficiency in treating wastewater, with mesoporous silica outperforming powdered activated carbon in adsorbing CFA. Activated carbon, however, exhibited better adsorption capacity for ACT and NAP, particularly at pH 5. Hydrogen bonds and electrostatic interactions were identified as possible mechanisms for silica's higher adsorption capacity.

Activated Carbon [13-15]: Activated carbon, with its extensive surface area and micropores, is a valuable tool for removing pharmaceutical contaminants from wastewater. The effectiveness of this method depends on the properties of the activated carbon, which can vary based on the preparation technique and raw materials used.

In conclusion, various methods, including photocatalytic degradation, biodegradation, biofiltration, adsorption, and activated carbon, have been explored to combat the presence of pharmaceutical residues in aquatic environments. Each

approach offers unique advantages and considerations in addressing this environmental challenge.

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 604m^2/g, total pore volume 12,7cm^3/g and average micropore radius 870Å.

2.2. Adsorption studies

Adsorption experiments were performed using wastewater having three different concentrations of anti-inflammatory drugs (1mg/L; 5mg/L and 10 mg/L), at two pH values (4 and 6) using three quantities of activated carbon material for the adsorption process (0,1g, 0,5g and 1g). All experiments were carried out in Erlenmeyer flasks using 100 mL of wastewater solution, homogenized using an 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 presence of pollutant residues in synthetic wastewater was assessed using the Total Organic Carbon (TOC) technique. Another effective method for quantifying the organic constituents within wastewater is also TOC, particularly suited for detecting low concentrations of organic matter. This TOC analysis involves introducing a known volume of the sample into a high-temperature furnace or chemically-oxidizing environment. In this controlled setting, organic carbon is transformed into carbon dioxide with the assistance of a catalyst. Subsequently, the carbon dioxide generated is accurately quantified using an infrared analyzer. Prior to analysis, the sample undergoes acidification and aeration, which serves to eliminate any potential errors stemming from the presence of inorganic carbon. This test can be conducted swiftly and is gaining popularity as a reliable method for assessing organic matter in wastewater.

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.

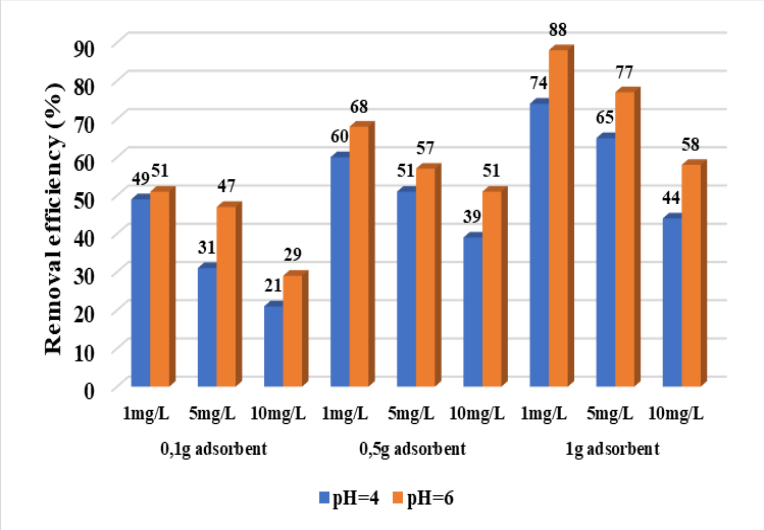

Fig. 1a. The effect of the pH on the acetaminophen drug residues removal at different concentration and adsorbent dosage

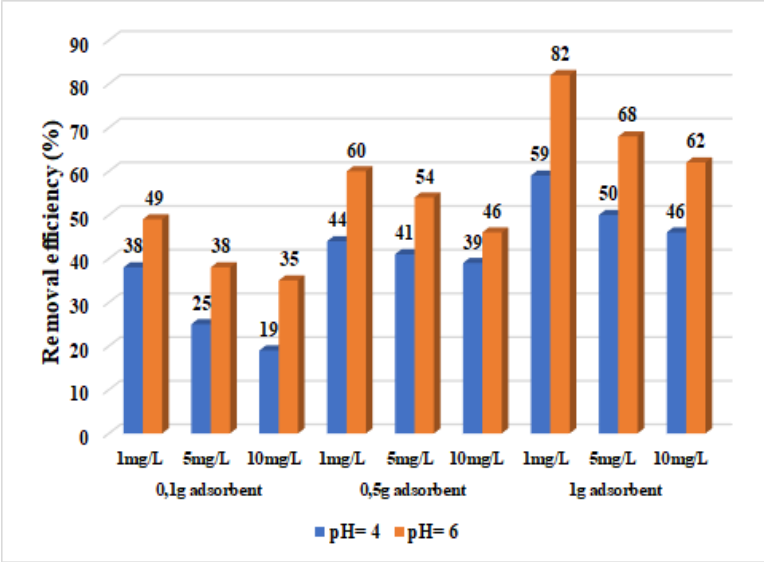

Fig. 1b. The effect of the pH on the diclofenac drug residues removal at different concentration and adsorbent dosage

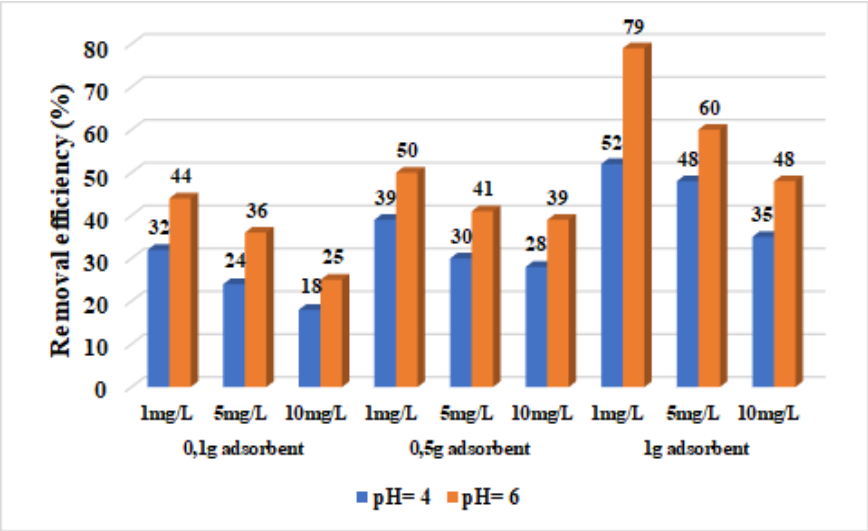

Fig. 1c. The effect of the pH on the ketoprofen drug residues removal at different concentration and adsorbent dosage

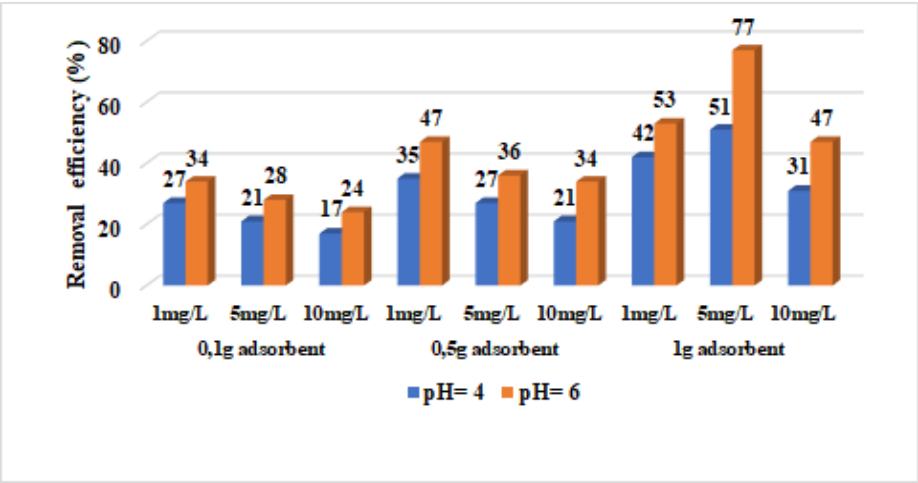

Fig. 1d. The effect of the pH on the ibuprofen drug residues removal at different concentration and adsorbent dosage

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 shown in Fig. 1a to Fig. 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%).

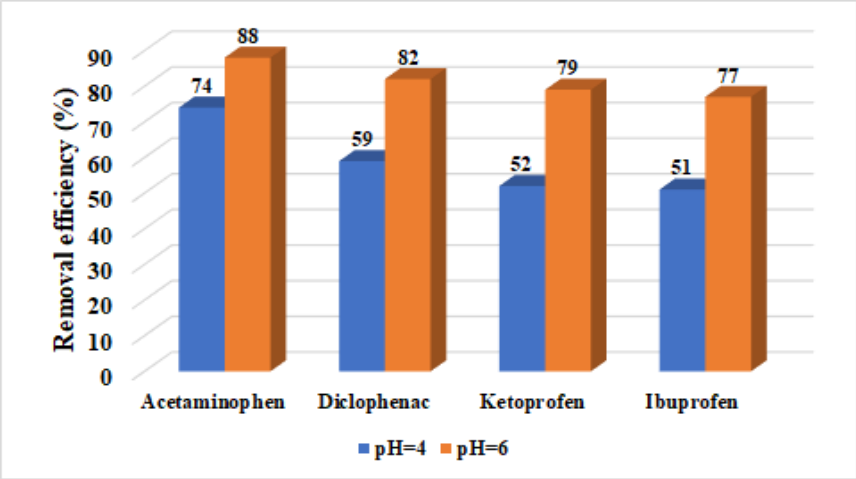

Fig. 2. The effect of the pH on the drugs residues removal at different pollutants concentration and adsorbent dosage

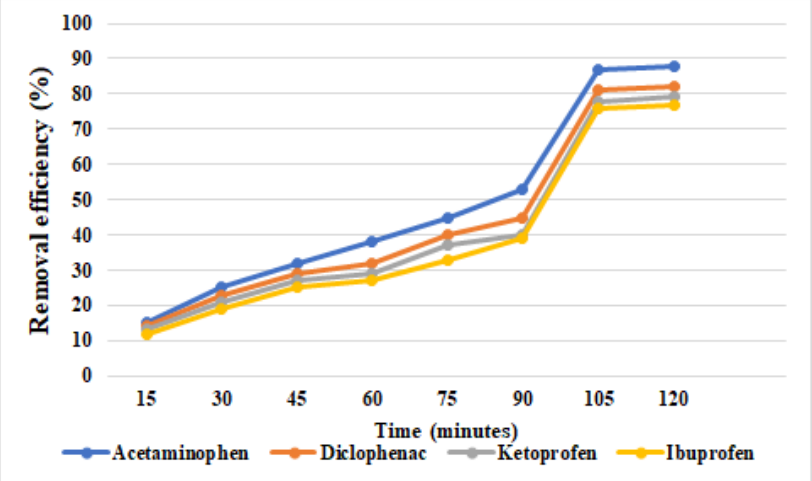

Fig. 3. Removal efficiency versus contact time

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].

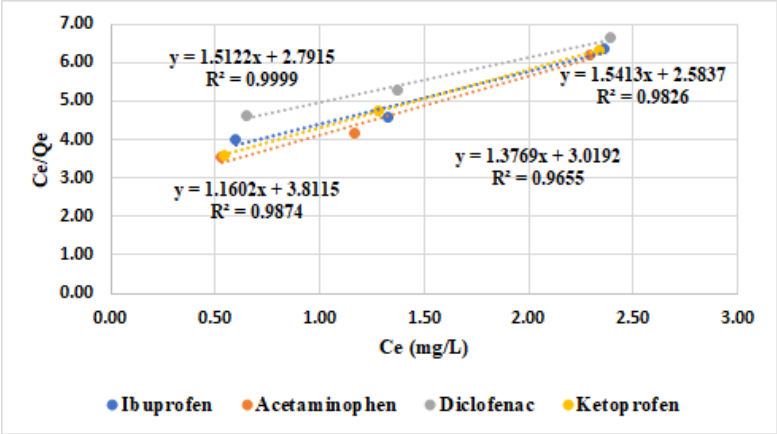

Fig. 4. Langmuir linearized isotherm for drug residues adsorbed onto activated carbon material

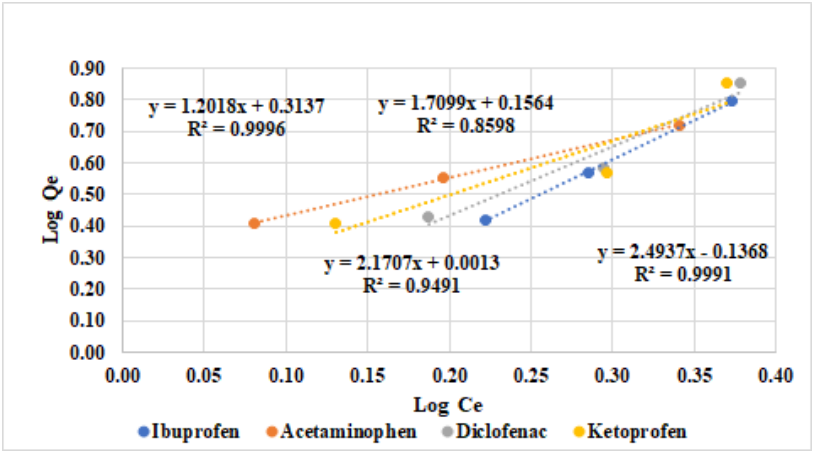

Fig. 5. The Freundlich isotherm for drug residues adsorbed onto activated carbon material

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:

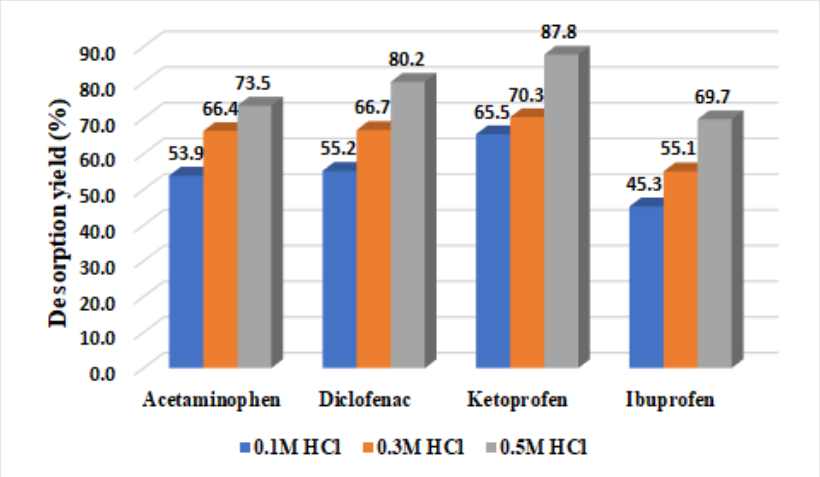

Fig. 5. The desorption studies

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 with legislation in force.

Following the experiments detailed in this article, it was observed that the highest level of efficiency in eliminating drug residues from synthetic wastewater was achieved. Specifically, when dealing with synthetic wastewater having a pH of 6 and utilizing 1g of adsorbent material, a treatment duration of 120 minutes was required to reduce the initial drug residue concentrations of 1mg/L. To analyze the adsorption processes, two mathematical models were employed. Judging from the correlation factor (R2), it can be deduced that the Langmuir model is a suitable fit for the data pertaining to diclofenac and ketoprofen, while the Freundlich model provides a good fit for the data associated with 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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