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Investigation of synthetic hospital wastewater treatment: elimination of Ketoprofen by cyclodextrin and photodegradation

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Abstract. To synthesize drugs is the objective to save humanity from diseases and epidemics. On the other hand, we must find a way to get rid of it without harming nature and life on earth. In this work we are interested in the issue of drug releases in hospital waters, where there are a lot of drugs used et encore les different microoganismes. Hospital wastewater (HWW) contains pathogenic agents and hazardous compounds; so, it will cause many risks on environmental and human health of different communities. Conventional water treatment technologies are not very effective for reducing the concentration of these pollutants to a desirable level. The aim of this work was to evaluate the efficiency of two technologies in reducing the pollutant concentration of two wastewater samples. Therefore, inclusion complex with native β-cyclodextrin (β-CD) were studied and their elimination capacities from water were evaluated. An emerging photodegradation process using UV lamp 365nm was also evaluated. For both technologies, we observed a decrease in the total Ketoprofenid Drug (KD) content due either to the inclusion and precipitation of KD by CD or to the degradation of KD under UV irradiations.

Keywords: Hospital wastewater, cyclodextrin, photodegrdation, ketoprofenid, UV irradiations, inclusion complex

1 Introduction

The quality of hospital wastewater is similar to municipal wastewater, but the effluent of hospitals wastewater may contain non-metabolized pharmaceutical compounds, antibiotics, disinfectants, anesthetics, radioactive elements, X-ray contrast agents and other persistent and dangerous compounds [1]. In the current era of human life, we have been facing an increased consumption of Non-Steroidal Anti-Inflammatory Drugs (NSAIDs). Nevertheless, NSAIDs are not

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completely metabolized by humans and are further excreted into domestical effluents. Several studies have been showing that a wide variety of pharmaceuticals are present in water effluents and are thus a matter of serious concern in the public health. Although treatment plants use sophisticated technologies for pollutants/contaminants removal, none of these processes was particularly designed for NSAIDs [2]. In this perspective, this work addresses the study the elimination of one of (NSAIDs) wich is Ketoprofen from water by two methods the inclusion with CD and photodegradation.

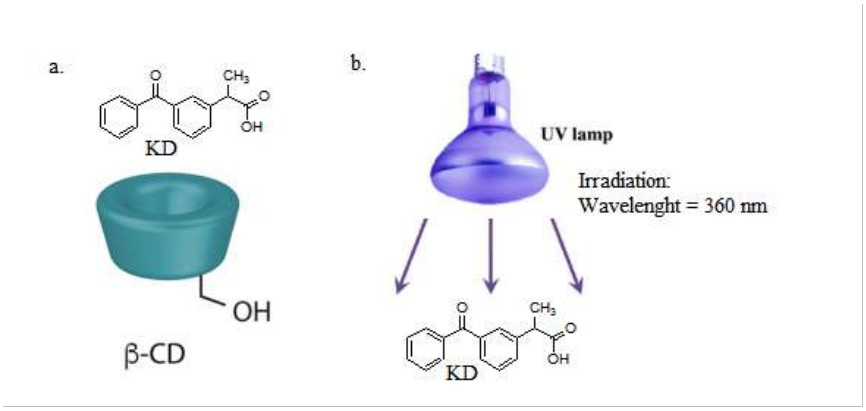

Fig. 1. Experimental apparatus: a – Inclusion complex KD-CD; b – UV light lamp.

In addition the pharmaceuticals compound have become an important issue for aquatic ecosystems and human health recently, because these compounds are biologically active substances and resistant to biodegradation in the ecosystem [3] Concern is growing over the contamination of the environment with pharmaceutical residues, among which non-steroidal anti-inflammatory drugs (NSAIDs) are one of the most abundant groups. Their widespread appearance in the aquatic environment is because of their high consumption and their incomplete removal during wastewater treatment [4].

The presence of Non-steroidal anti-inflmmatory drugs (NSAIDs) in drinking and superfiial waters is a major public health [5] since little is known about the potential chronic effect on human health associated with the long term ingestion of mixtures of these substances . The problem is felt even more in the case of water reuse, since (NSAIDs) are persistent, toxic, bio-accumulative and biorefractory [6].

Several methods have been used for drug extraction from environmental wastewater [7], such as photodegradation [8], nanofiltration and ultrafiltration [9], ozone oxidation [10], electrodialysis membrane [11], and coagulation-floculation and flotation [12]. Most of these techniques suffered either from technical or economic problems.

Native or polymerized CDs [13] are widely used as a carrier in affinity membranes for the removal of contaminants such as heavy metals, and hydroquinone [14, 15]. The characteristics of an effective adsorbent include selectivity, high adsorption capacity, long lifetime for use, and availability in large amounts at low cost. Much effort has recently been focused on various materials based on polysaccharides like cyclodextrins (CDs) [16]. CDs are a family of cyclic oligosaccharides that are composed of a-1,4-linked glucopyranose subunits [17] . The most common CDs are of three types: α-cyclodextrin (α-CD), β-cyclodextrin (βCD) and γ-cyclodextrin (γ-CD), composed of six, seven and eight glucosyl units, respectively. CDs have a hydrophilic outer surface and a hollow hydrophobic interior [18] (Fig. 2) .

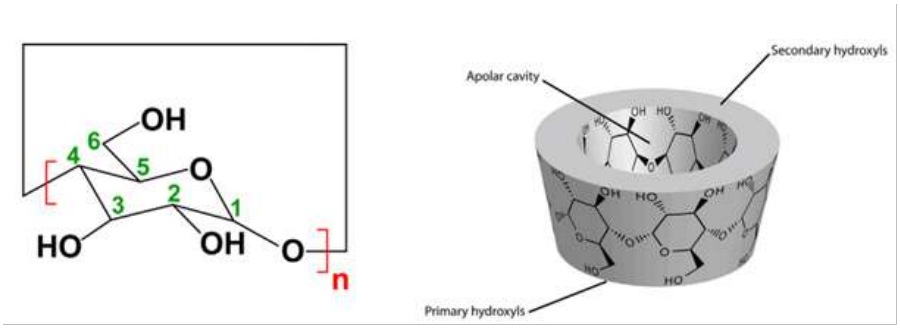

Fig. 2. Chemical structure of $\alpha - CD(n = 6), \beta - CD(n = 7) and \gamma - CD(n = 8)$.

In fact, the chair conformation of the glucopyranose units makes cyclodextrin molecules have the shape of a truncated cone with a central cavity. The external surface is hydrophilic because of the presence of hydroxyl groups, which are oriented towards the cone exterior with the primary hydroxyl groups at the narrow edge of the cone and the secondary ones at the wider edge. The presence of the skeletal carbons and ethereal oxygens of the glucose residues gives a lipophilic character to the central cavity. The type of structure provides to the cyclodextrin the ability to form water-soluble inclusion complexes with guest hydrophobic molecules of suitable size [19].

Recently, β-cyclodextrin (β CD)-based polymers with enhanced adsorption kinetics and high removal capacity of organic micropollutants (OMPs) One promising building block is β-cyclodextrin (βCD), which is an inexpensive, nontoxic, naturally occurring cyclic oligosaccharide produced from starch [21].The aim of this work was to prepare CD extraction of KD from waterwaste, and to compare its efficiency to photodegradation KD under UV irradiation lamp 360nm. Among many adsorbent, there is a general consensus among researchers that the commercial CD is superior because of its water sollubility, large stability to light illumination, low price and nontoxicity.

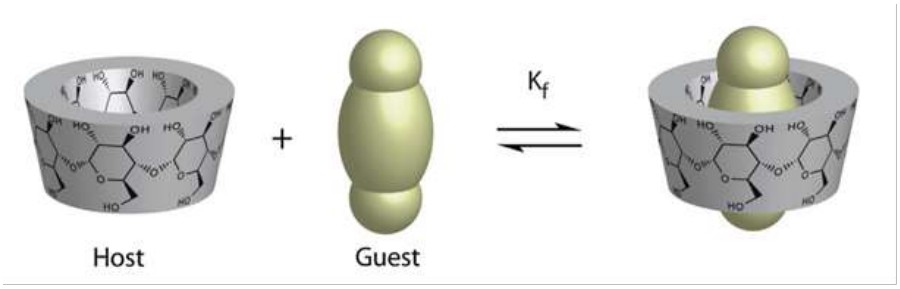

Fig. 3. Cyclodextrins structure and inclusion complex formation [20].

Other method very useful: the UV irradiation is often employed for disinfection of drinking water and municipal wastewater treatment plants (WWTP) [22], and it has also been demonstrated to effectively reduce the concentration of recalcitrant organic compounds [23, 24].

The compound selected for this study was widely used pharmaceutical compounds with different chemical structures: ketoprofen (non-steroidal anti inflammatory drugs). These compounds were found in relatively high concentrations (up to 21.6 g L1) [25,26] in the effluent of the secondary settler of municipal WWTPs, thus reaching a subsequent disinfection process. The photolysis of ketoprofen has been previously investigated, mostly in distilled water and surface water matrices [27, 28]. UV photolysis can be strongly affected by the presence of other organic compounds, or particulate matter. In the present study, the photodegradation kinetics of ketoprofen, was assessed in with a UV lamp 360nm, in pure water.

2 Materials and Methods

2.1 Reagents

β-cyclodextrin (β-CD) was obtained from Prochima (Aldrich, 99.8%). KD from pharmacy were used as received.

2.2 Synthetic Wastewater prepation:

In order to develop a method for the treatment of hospital water, we have prepared a model solution of precise concentration 0,01g/L which represents hospital effluent. Because given the means of our laboratory, it is impossible to handle real hospital water with all that includes microorganisms and other potentially harmful releases. The UV-Visible spectrophotometer used in this study is a Thermo-Scientific Heλiosγ.

2.3 Drug use:

We chose the drug Ketoprofen 100mg, an anti-inflammatory widely found in hospital waters and which escapes to the traditional treatment of plants.

2.4 Procedure of treatment KD solution by (β-CD):

NMR spectra were recorded at 25 °C in CDCl3 (0.004mmol.L-1) on a Bruker 500, 400 or 300 MHz instrument, using tetramethylsilane (TMS) as an internal (ppm) and coupling constant (standard. Chemical shifts are given in J) values in Hertz (Hz). I.R spectra were collected from a Mattson Genesis II FTIR. To 20 ml of the diluted solution (10^3 g/L) are taken in an Erlenmeyer flask and 0.1 g of (β-CD) is added. This solution is left stirring at room temperature for 4 h. The solution is filtered and analyzed with a UV-Visible spectrophotometer with an interval of [200 to 370] nm.

2.5 Photodegradation experiments:

Photodegradation experiments were carried with one UV lamps of $\lambda = 360$ nm . To the vessel containing 20 mL of synthetic wastewater under stirring under irradiation and aliquots of solution were collected at 15-min intervals. The aliquots were immediately analyzed using a Thermo-Scientific Heλiosγ analyzer.

3 Results

3.1 The treatment KD solution by (β-CD):

From the results obtained, presented in Fig. 4. We can see that β-CD had a good affinity for KD, and that aromatic derivatives are better recognized by CDs that aliphatic ones. These results are in good agreement with the values of the formation constants of the inclusion complexes.

3.2 Photodegradation process of the KD in water solution:

Direct photolysis can only take place when a compound is able to absorb light at the wavelengths to which it is exposed. The photodegradation treatment of KD solution by UV irradiation was followed by a record of the KD Absorbance as a function of time (Fig. 5).

In a second part, we carried out a kinetic study of the photodegradation of the KD solution in pure water, with a UV lamp of 360nm. The results clearly show the degradation of the KD.

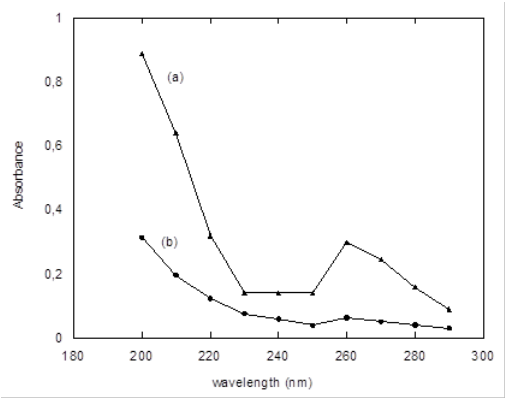

Fig. 4. UV spectra at 260nm of (a) Ketoprofen,(b) Ketoprofen+cyclodextrine.

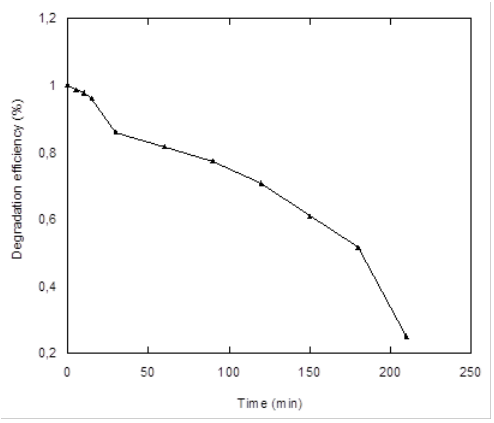

Fig. 5. Photodegradation of KD solution under UV irradiation.

4 Discussion

The formation of inclusion complex insoluble in water, give β-CD material is an interesting process to remove KD or other aromatic drugs before the release of wastewater into the environment. After the process, the -CD material could be regenerated by ethanol washing or eliminated by incineration, thus avoiding the need for fastidious and expensive regeneration. We investigated the encapsulation of many synthetic derivatives compound in commercial CD and calculating the association constant and determining some dynamic aspects of the complexation process. It was of interest to find a model compound derivative complexed with CD in our laboratory [29]. The results and conclusions can hardly be extended to other classes of compounds as drugs [30]. Therefore, we needed an accurate identification of protons that were sensitive to complexation in order to prove the KD-CD complex. The binding of β- of KD CD was evidenced by

a shielding of internal cyclodextrin H-3 and H-5 protons. The chemical shifts of the remaining H-1, H-2 and H-4 protons of the same host were not altered, as already shown by Topai and Col.,. βCD internal protons is selective and exclusive effect of complexation on the generally taken as good evidence for an interaction, where KD is encapsulated in the CD. It can be attributed to the magnetic anisotropy associated with hydrophobic core of the βCD and the aromatic ring of the KD.

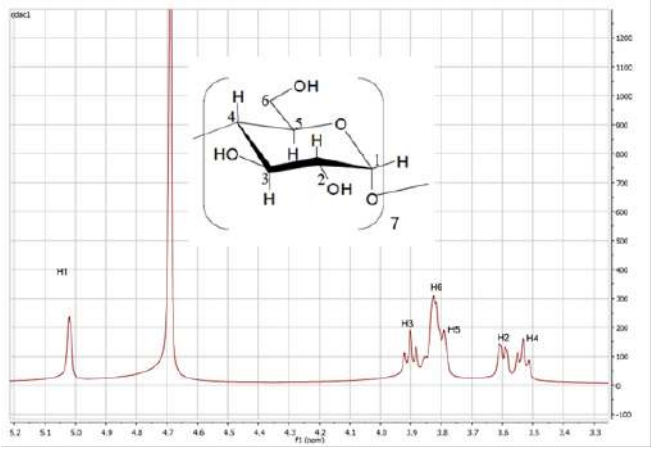

Fig. 6. 1H-NMR spectra of CD in D2O.

The formation of inclusion complex of CD and a guest substance is accompanied by changes in their IR spectra as compared with the individual components [31].

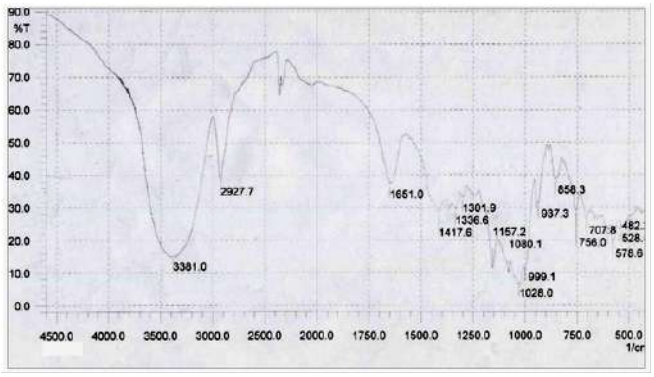

Fig. 7. IR spectra of CD.

We observed a considerable decrease in the concentration of the drug which proves the effectiveness of this method in making the drug precipitate and then it filtration from the solution. The inclusion of KD into -CD [32] has been investigated by NMR spectroscopy, was reported by M. Paci and Col.,. Structural details have been studied by resonance assignments and by measuring KD chemical shift variations related to changes in the magnetic anisotropy of mutual orientation(s) of aromatic rings and the carbonyl moiety of KD [33]. In the other hand, Several studies [34,35,36] have been performed to elucidate the photochemistry of KD under a variety of conditions and by different experimental approaches. The reported results indicate that irradiation of KD in neutral aqueous medium gives rise to 3-ethylbenzophenone, which undergoes fast transformation into more stable hydroxylate products. The mechanism of the decomposition pattern has also been investigated in detail [37,38, 39].

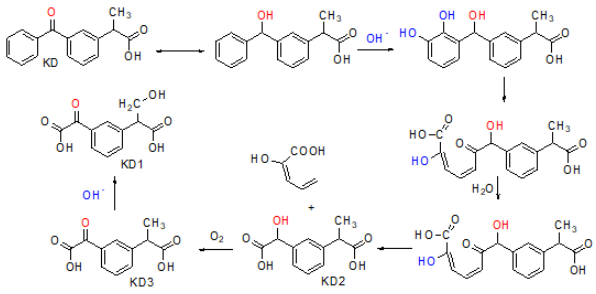

Fig. 8. Proposed UV photolysis pathway of KD.

The pathway proposed for KD degradation by direct photolysis is presented in Figure 8. Oxidative ring opening of the catechol by meta-cleavage would yield a hydroxymuconic semialdehyde. By the subsequent hydrolysis, a hydroxy pentadienoic acid and product KD2 are formed. Finally, the secondary alcohol in product KD2 would probably be readily oxidised to form product KD3 under the UV radiation conditions of this experiment. Of the 16 carbon atoms of the ketoprofen molecule, five carbons would be split as -hydroxy pentadienoic acid, a mechanism that was previously described by Carvalho and col [40], and Quintana and Col [41].

5 Conclusion

Our developed work, within our laboratory at the university center of Maghnia. Represent a small scale test that we want to apply on a large scale. A preliminary investigation concerning the degradation of KD in water via direct UV-light irradiation was carried out; a lab-scale expirment with a lamp emitting monochromatic UV-light at a wavelength of 360 nm, was used. In particular, the

effect of the irradiation time was investigated. This study clearly demonstrated the suitability of the βCD to be used as an adsorbent for the removal of KD from wastewater. These two processes (complexation and photodegradation) could be used consecutively. Adsorption could be used to concentrate the KD and then it photodegradation.

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