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Using titanium oxide membranes and ultraviolet (UV) light to remove pharmaceutical waste from hospitals wastewater

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Abstract
In recent years, the accumulation of pharmaceutical waste has become a major global concern; diclofenac sodium is one of these drugs that commonly used as a non-steroidal anti-inflammatory. the conventional wastewater treatment and drinking water production processes used to remove pharmaceutical waste from liquid waste before discharge, but it is not efficient to remove a wide range of pharmaceutical compounds. TiO_2 nanofilm membranes were used on fixed glass panels as an alternative to the traditional form to assess its efficiency in removing pharmaceutical contaminants from wastewater. In this study, the effect of TiO2 thin films as a photocatalyst for oxidation has been studied in removing diclofenac sodium from contaminated water Through studying the effect of reaction time and pH value. The reaction time varied from 0 to 120 minutes with different concentrations of diclofenac sodium samples (10, 20, 30, 40 and 50 ppm). There was noticeable effect in the first 10 minutes and a rapid removal of diclofenac sodium concentration in the sample at a rate of (20%). Also Changing pH value affects the removal rate of diclofenac sodium, it was observed that the lower pH value, the higher the removal of diclofenac sodium.

Keywords: Pharmaceuticals, Wastewater, Water treatment, Advanced oxidation processes, Photocatalysis, titanium dioxide.

Introduction
In recent years, a large number of medical contaminants and pharmaceutical preparations have been detected at different concentration levels in the aquatic environment (groundwater, surface water and even drinking water sources), this issue is getting concerns due to the potential risks on aquatic life and human societies, on the other hand studies have shown Clearly, the inefficiency of conventional wastewater treatment and drinking water production processes in removing a wide range of pharmaceutical compounds()Kümmerer et al., 2004; Kumar and Xagoraraki 2010(). Oxidation is one of those treatments used to remove pharmaceutical compounds, and oxidation is defined as the transfer of one or more electrons from the donor elements (reduction) to the accepting element (oxidant) which has a higher affinity for the electrons. These electron transfers lead to the chemical transformation of each of the substance Reducing and oxidizing, and in some cases producing chemical types with an individual number of valence electrons, these types known as "effective free radicals", tend to be largely unstable, and are therefore highly reactive because one of their electrons is not coupled (Marcus, 1956). Advanced Oxidation Processes include two stages, the first stage is the formation of strong oxidizers (such as hydroxyl radicals OH) and the second stage is the interaction of these oxidizers with water contaminated by organic and inorganic pollutants. However, the term advanced oxidation processes refer to the processes in which oxidation of organic pollutants occurs mainly through reactions with hydroxyl radicals (Azbar, Yonar et al. 2004).The oxidation reactions that produce free radicals tend to be followed by additional oxidation reactions between the free radicals oxidizers and other reactants (organic and inorganic) until stable oxidation products are formed by thermodynamics, the oxidizer's ability to initiate chemical reactions is measured in terms of the oxidation voltage. the end

products For complete oxidation, organic compounds are carbon dioxide (CO_2) and water (H_2O) (Clerici and Ingallina ,1998). In water treatment applications, AOPs usually refer to subgroups of processes use O_3, H_2O_2, with / or UV ... etc., however in the field of medical pollutant treatment, AOPs will be used to refer to a set of processes that also include TiO2 stimulation, Stimulation, cavitation, electron-beam irradiation and Fenton stimulation, where All of these processes can produce free hydroxyl radicals, which can interact with a wide range of organic pollutants and destruct them)Kow, Fahmi et al. 2016(. TiO_2 is one of semiconductors with relatively high energy gap)Karabay, Yüksel et al. 2012(, it was studied in a wide range and recommended as the best catalyst that eliminate environmental concerns due to its inertness, non toxicity, low cost production, optical stability and strong optical stimulation (Tian, Zhao et al. 2014), in addition to excellent decomposition of contaminants an biological stability (Toloman, Pana et al. 2019).Thin films TiO2 have proven their importance due to their multifunctional applications including photocatalytic, hydrophilic materials, photoelectric cells, color and photoelectric devices, gas sensor, biosensor, corrosion protection and water separation (Mahlambi, Ngila et al. 2015), However, there are still some defects that limit the use of titanium as Optical catalyst one of which is the rapid re-union of electrons with gaps of low quantum return and photon induced charge carriers, the other is the presence of an energy gap in TiO2 very wide (3.2 and 3.0 eV for Anatase and Rutile, respectively), so it can only be activated only in the ultraviolet region Violet which accounts for only 4-5% of the solar spectra (Zhou, Yan et al. 2019).The continued discharge of pharmaceutical compounds into the aquatic environment has caused increasing concern about the presence of these new emerging pollutants, and of their potential impacts on aquatic ecosystems and human health even at a low concentration Schwarzenbach, (Escher et al. 2006).pharmaceutical compounds come from various sources in the aquatic environment, but the main ones are drugs that are highly consumed by humans or animals, as well as improper disposal of unused or expired medicines that are released into wastewater from drug manufacturing factories, hospitals and homes)Khetan and Collins 2007; Trapido, Epold et al. 2012; Yu, Nie et al. 2013(.These pharmaceutical pollutants and their metabolites end up in the sewage system and access to treatment plants (wastewater treatment plants), which have proven to be incompetent to remove drugs from wastewater and thus release liquid waste to water bodies, and as a result they are detected in a wide range From samples including surface water, groundwater and drinking water)Bendz, et al. 2005; Klavarioti, Mantzavinos et al. 2009; Behera, Kim et al., 2011). Among the various drugs, non-steroidal anti-inflammatory drugs were focused on because they are the common pollutants present in the aquatic environment due to the high consumption of these drugs. Diclofenac sodium is a common substance used in non-steroidal anti-inflammatory drugs, in medical care mostly used as analgesic in the name of sodium salt, and it is estimated the amount of Consume it with hundreds of tons per year worldwide (Buser, Poiger et al. 1998).

The research aims to study operational conditions (reaction time, primary concentration and pH) on the efficacy of removing pharmaceutical contaminants from contaminated water using advanced oxidation technique with ultraviolet radiation in the presence of TiO2.

Mechanism of reaction: Photocatalytic reaction is a chemical reaction that occurs under the combined effect of light and photocatalyst. This technology has many advantages, including environmental protection, the complete decomposition of pollutants. Figure 1 shows the basic principle of photocatalysis.

From the view of semiconductor photochemistry, photocatalysis action is the light-induced oxidation reactions of semiconductors. The semiconductor has a power packet structure consisting of low energy valence band (VB) and high energy conduction (CB) band, the band gap between the conduction band and the valence band is called the restricted band.

When the energy of the incident light is greater than the semiconductor band gap, the electrons in the VB of the semiconductor are irradiated to CB by photons, and the corresponding gaps generated in the VB. The electrons and gaps generated by light are separated by the electric field and transferred to the surface of the semiconductor molecules.

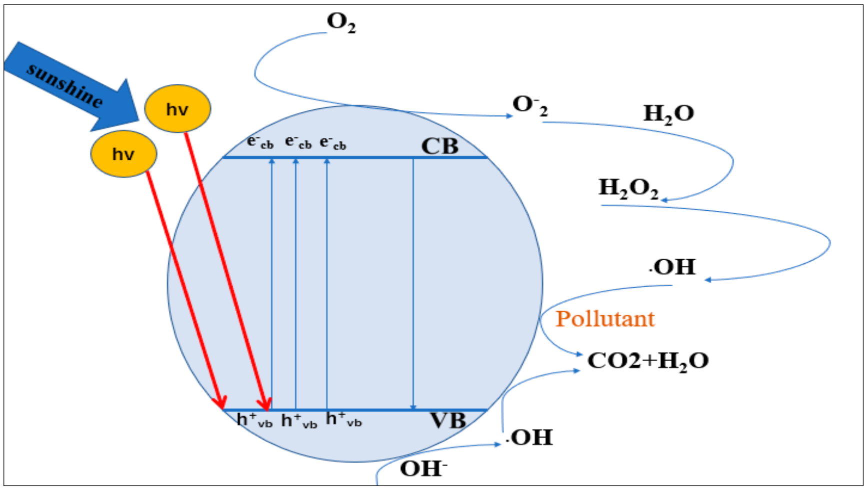

Figure (1): mechanism of photocatalyst reaction (Zhang, Wang et al. 2019)

The photosensitive pores have strong oxidizing properties and can oxidize the materials absorbed on the surface or solution from the semiconductor. The detailed steps of the photocatalytic reaction are as follows, under the influence of a specific energy of light irritating the electrons present on the VB and leaping to CB, and the gaps remain on the VB. Electrons on CB travel to the catalyst surface and participate in the reduction reaction, and the gaps in VB are displaced on the surface of the photocatalyst and participate in oxidative reactions. In the reaction path, electrons can form H2O2 or super free radicals of O2 with H + and dissolve O2 in the aqueous solution, and thus the gaps can oxidize OH to produce hydroxyl radicals that have the ability and influence to break down pollutants (Zhang, Wang et al. 2019).

Materials and Methods

1-TiO_2 nano thin film: TiO_2 nano thin film were deposited on glass slides with a dimension of (25 x 75) mm, using Chemical Bath Deposition (CBD). This method is carried out by heating the titanium acid (III) solution, and then adds 4 ml of liquid $TiCl_3$ to 100 ml distilled water and mix the solution. After that, adjust the pH to 0.7 by adding the urea solution (NH_2CONH_2) with continuous stirring and at laboratory temperature (25°C) for one hour to obtain a homogeneous violet solution (YU, Yu et al. 2003). Scanning Electron Microscope (SEM) was used to image morphology of TiO_2 thin film surface, Figure 2 shows the completely covered slide with spherical nanoprticles of 64-120 nanometer TiO_2, this form provide a large surface area.

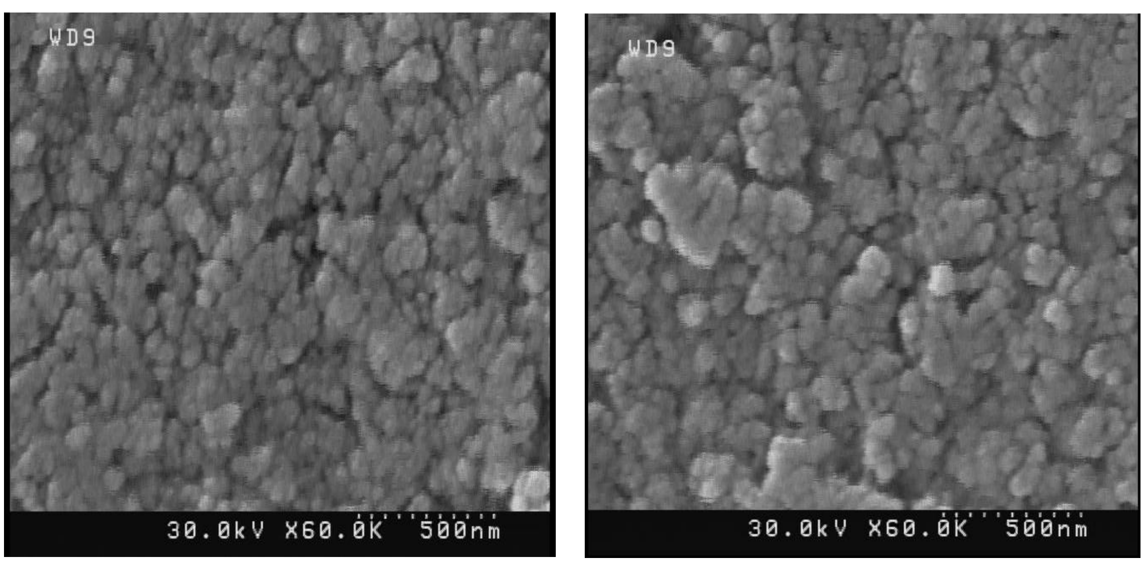

Figure (2): SEM image of TiO_2 thin film (top view)

2- The laboratory treatment system consists of a glass column containing contaminated water with UV lamp (6 w) in the middle and two slides of glass coated with a thin film of TiO2, installed on both sides of column. magnetic stirrer used in order to stir the liquid at specific speed as shown in Figure 3.
3- Diclofenac sodium with a concentration of 100 mg, manufactured by acino.
4- pH meter manufactured by WTW company.
5- UV- Spectrophotometer manufactured by Shimadzu Corporation.
6-Calibration standard solutions.
7-chemicals (NaOH, HCl).

Atotal of 350 ml Diclofenac sodium with a concentration of 100 mg was used to prepare laboratory samples in different concentrations (10, 20, 30, 40, 50 ppm). The samples concentrations were examined by a UV-Spectrophotometer at a wavelength of 276 nm. The glass slides on which the titanium oxide were deposited were fixed vertically parallel to the UV lamp, then the sample was placed in the reaction column and was stirred by using a magnetic stirrer, Samples were taken from the reaction column by 5 ml every 10 minutes and at the rate of 12 samples during one experiment.

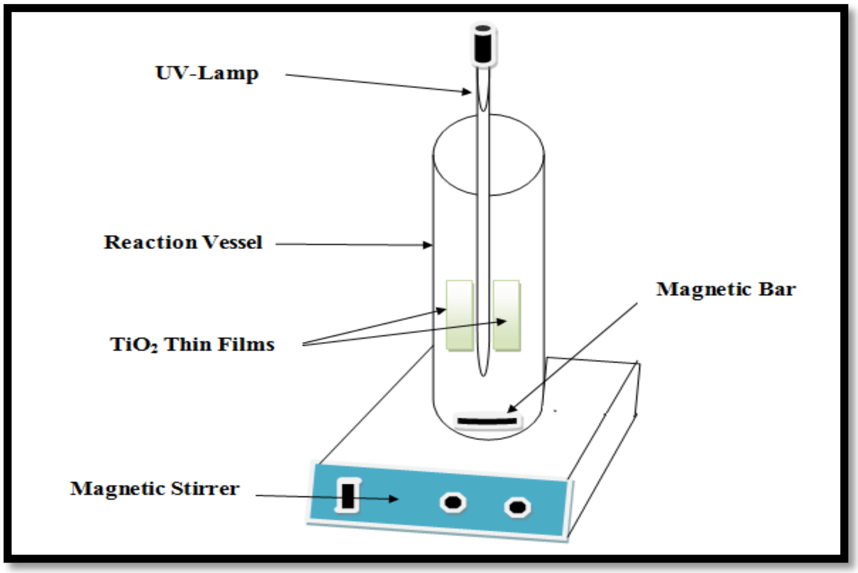

Figure (3): Components of laboratory system

Results and Discussion

The effect of ultraviolet radiation: The effect of TiO_2 membranes as a photocatalyst for oxidation with the use of ultraviolet radiation was studied on the concentration of diclofenac sodium for contaminated water by studying the effect of reaction time and changing the acidic function and the concentration of the pollutant, the reaction time was (0 to 120 minutes). The effect of photocatalysis of the TiO_2 membrane without exposure to ultraviolet radiation was studied with a contaminated water sample with a concentration of (10 ppm) which is the lowest concentration of contamination for laboratory experiments. From Figure (4) we can notice that the diclofenac sodium has been reduced but at a very small rate (about 2%) due to the fact that the energy gap of the TiO2 thin film is large (up to 3.2 volts), while the amount of UV radiation coming from the laboratory light is very low, This means that a few electron gap pairs will be generated, which in turn will form free radicals that interact with contaminants in water. After irradiation of the TiO_2 membrane by ultraviolet rays, we notice that during the first 10 minutes of the start of operation, a rapid removal of the percentage of diclofenac sodium in the sample was observed, at a rate of (20%) where the sample concentration (10 ppm), we note that the removal rate slows or remains Stable after that period of operation as a result of the formation of a thin layer on the TiO_2 catalyst, the optical removal process is reduced by stopping the oxygen supply to the catalyst surface.

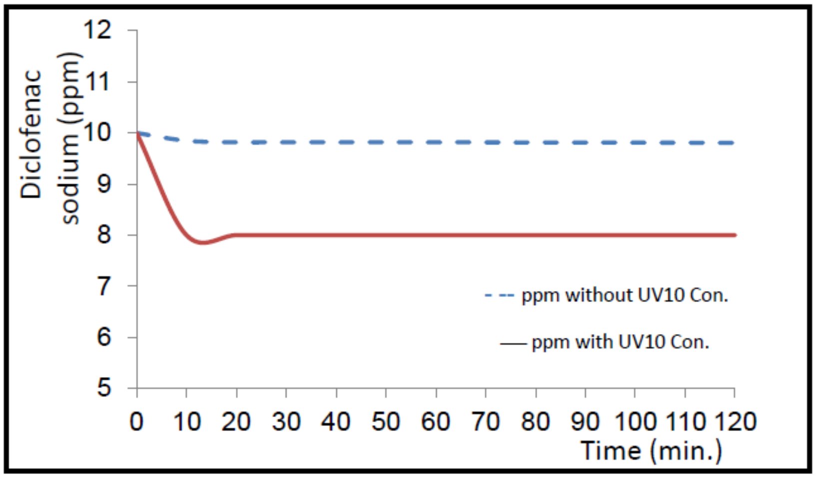

Fig. 4 Diclofenac sodium concentration over time using TiO_2 membranes

Primary concentration effect: Figure 5 represents the different concentrations used of diclofenac sodium where it was (20, 30, 40, 50 ppm) respectively. We notice that during the same operational time period and with the same surface area of TiO_2 nanoparticles, the removal rate during the first ten minutes of the start of operation was the highest and then begins to decrease and persist to the end of operation time (120 min.) Despite the different concentrations of sodium diclofenac, the removal rate was 1.8%, 2.4%, 3.7% and 7.5%, respectively. the reason for this may be that the excess of the contaminants in the water leads to the formation of a thin layer (a barrier between UV and the membrane) that slows Photo-curing process by stopping the supply of oxygen to the catalyst surface.

Effect of pH: The effect of pH on photolysis processes of diclofenac sodium has been studied in a range of pH (2-9). The pH of the treated samples is set before the start of the photocatalysis process not during the reaction. pH of the sample is one of the important factors in photocatalytic reactions that occur on the surface of TiO2 particles because it determines the properties of the surface of the photocatalyst and the size of the groups that compose it, and therefore The pH plays an important role in the reaction mechanism that can contribute to the processes of removing the contaminants, through the direct interaction between the hydroxyl formed by the interaction of the positive gaps and the direct reduction of the electron in the region of the conduction band, in the presence of the photocatalyst. photocatalysis processes are caused by electron ⁻ gap pairs formed on the surface of the semiconductor material exposed to ultraviolet radiation, where the gaps are considered to have a high oxidation potential, by two mechanisms: the first works directly on the oxidation of diclofenac sodium and the second interaction of these gaps with (OH-) To form the free radicals of hydroxyl, the electron in the conduction b also and participates in the reduction by forming H_2O_2 or free radicals. Figure (6) shows the effect of the change in the acidic function in the reaction column on the removal rate of diclofenac sodium with an initial concentration of (10 ppm), as it is the best concentration of treatment according to previous experiment. When the acidic function pH = 2, the removal rate is (26%), but if the acidic function pH = 4, the removal was (20%), while when the acidic function pH = 6 the removal rate was (16.8%), and finally when the acidic function pH = 9, the removal rate decreased to (8.9%). At pH = 2, we notice that the efficiency of TiO_2 membrane adsorption increases and begins to decrease as the acidic function increases until it reaches the lowest level in the basal medium pH = 9. The reason for this is due to the oscillating behavior of most semiconductor oxides where the pH reaction occurs on the surface of the semiconductor molecules and leads to dispersion and rapid removal of hydroxyl radicals with no time to interact with sodium diclofenac, in addition that it affects the surface charge properties of the photocatalyst, on the other hand Diclofenac sodium is charged with negative charge, so a low pH supports absorption on the catalytic surface.

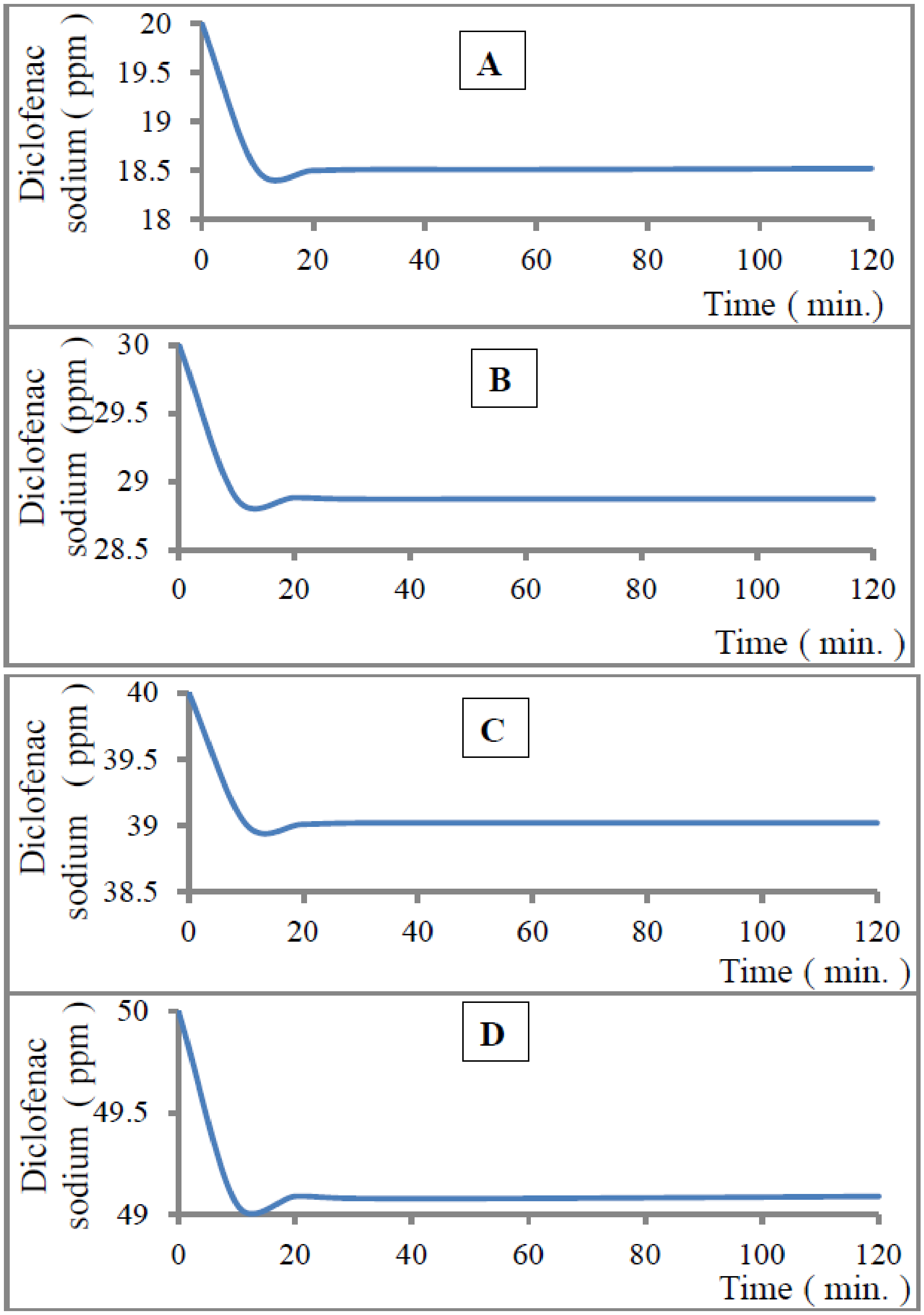

Fig.5 shows the removal rate of Diclofenac sodium with time using UV & TiO_2 with different primary conc.: (A) 20ppm (B) 30ppm (C) 40 ppm (D) 50ppm

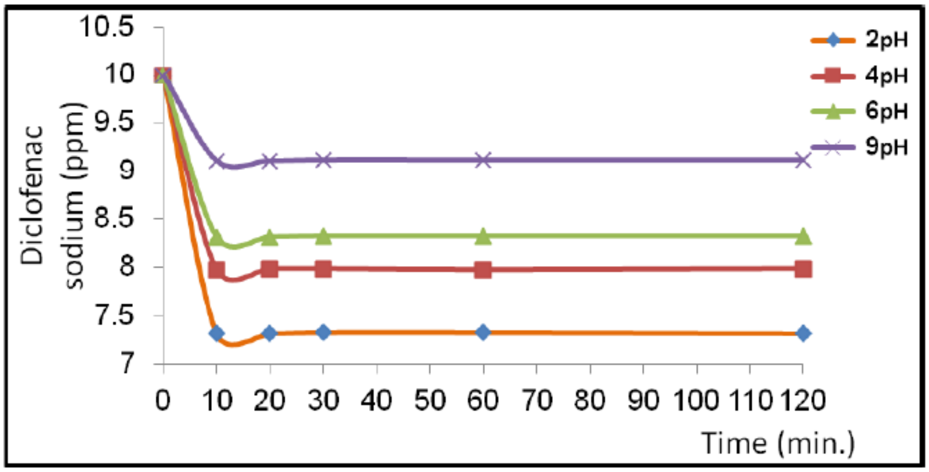

Fig.6 removal rate of Diclofenac sodium with different pH using TiO_2 & UV (initial concentration =10ppm)

Conclusions

The presence of drugs and pharmaceutical preparations in the aquatic environment causes health risks, although at relatively low concentrations, but it may represent a serious threat to the environment. Pharmaceutical preparations that are designed to be bioactive are usually lipophilic and resistant to biological degradation, and therefore the potential for accumulation in the environment. use of TiO2 membranes is one of the advanced oxidation techniques used to remove pharmaceutical preparations with noticing The following:

1- When UV rays used, the efficiency of the TiO2 membrane increases by 18%
2- There was a rapid removal of pollutants within the first 10 minutes of startup.
3- The efficiency of titanium oxide nanofilm has increased in the acidic solutions.
4- The efficiency of titanium oxide nanofilm has been better at low concentrations of contaminants.
5- Advanced oxidation by TiO_2 nanofilm is considered as echo friendly technique and can be combined with other techniques in order to reduce the concentration of pollutants to acceptable limits.

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