AN OVERVIEW ON THE APPLICATION OF PHOTOCATALYSIS FOR WATER PURIFICATION FROM PHARMACEUTICAL DRUGS

NINA KANEVA*, ASSYA BOJINOVA, KAROLINA PAPAZOVA

Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Bourchier Blvd., Sofia 1164
* Corresponding author: nina_k@abv.bg

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Abstract: The elimination of organic substances from surface and subsurface water/wastewater is a subject of environmental significance. Conventional water decontamination approaches have relatively higher operating costs and cause the formation of by-products, which may be more toxic than parental contaminants. On the other hand, heterogeneous photocatalysis is one popular and eco-friendly method. The treatment of wastewaters by photocatalysis using metal oxide semiconductors is a topical issue. In recent years, zinc oxide has attracted attention in the scientific community as a "material of the future." The advantages of nanostructured ZnO as a photocatalyst have prompted the creation of a number of methods for its synthesis. Furthermore, the non-toxic nature of ZnO nanomaterials means they are convenient for water treatment, resulting in safe drinking water for humans and a safe environment for animals. Therefore, this semiconductor has a very large application in environment cleaning, particularly for photocatalytic degradation of pharmaceuticals. Pharmaceuticals are emerging pollutants that are increasingly found in water systems – marine, estuaries, rivers, lakes, and underground water around the world, with concentrations ranging from ng/L to μg/L, and even reaching mg/L. In this review, the degradation of various pharmaceutical drugs in drinking water/wastewater is discussed. Various methods of zinc oxide synthesis for improving the photocatalysts efficiency are presented. The effects of the different experimental parameters on the photocatalytic processes are compared and commented

INTRODUCTION

The availability of fresh water is crucial for maintaining a vital activity - drinking, cooking, cleaning, agriculture, etc. Nature has its own mechanism for recycling water to provide enough fresh water of high purity. However, modern human activities have disrupt the balance between use and natural purification processes and led to a shortage of drinking water. It has been found that most of the natural resources of drinking water are contaminated with various toxic contaminants and pathogenic microorganisms (Chen et al. 2021). This leads to water shortages for 700 million people worldwide. It is estimated that this problem will affect 1.8 billion people by 2025 (UNDESA, 2005-2015). According to a report by the World Health Organization, water-borne diseases kill nearly 12 million people each year (UNDESA, 2005-2015). About 90% of all diseases found in developed countries are related to the consumption of polluted water (Baruah et al. 2009). There are nearly 4 billion reported cases of diseases caused by polluted water in the world. The contaminants (dyes, hormones, pesticides, pharmaceutically active compounds, personal care products, etc.) come from various sources such as industries, agriculture, pharmaceuticals and many others. The demand and consumption of such products increases and this subsequently raises their concentration level in the water due to improper disposal and effluents from municipal and industries (Sabouni et al. 2019). Among the emerging pollutants are pharmaceutical drugs. In general, pharmaceuticals are poorly absorbed by both humans and animals. Their discharge of fecal, urinal and contaminated wastewater are potential threats to the ecosystem.

The development of industrial technologies and the inclusion of new capacities make water a "key problem" for the existence and protection of mankind. Modern civilization poses an extremely important problem to the environment - the reduction of water resources and their pollution.

The main water pollutants can be divided into two categories depending on their source. Pollutants that enter the water from separate sources, such as water discharged from treatment plants, factories and production facilities, leaking underwater warehouses, etc. The second group of pollutants is those that do not originate from individual points of pollution, but are global or act on a larger scale, such as nitrates mixed into agricultural land after rain or heavy metals and other impurities in heavy traffic areas where the burns gases are mixed with rainwater, etc. Most of the pollutants are found in nature, the main criterion by which they are determined is their concentration in a given environment. Even with low concentrations, they are considered to be polluting. Water pollution is a global problem. Water pollution from industry is primarily due to the chemicals used or produced in the industry. Some of them have bactericidal properties and change

the normal flora and fauna of water bodies. Most of these chemicals are toxic and dangerous to human health. The rapid pace of industrial development, the lack of a sufficient number of treatment plants, the poor operation and frequent accidents in them, the lack of reverse cycles for the use of industrial water - these are the main reasons leading to increased water pollution. The main water intakes of polluted industrial wastewater are rivers and lakes. Rivers, in turn, cause pollution of the seas and the world's oceans. Many rivers have become dead waterbeds and canals with contaminated dirty water, creating the conditions for the spread of epidemics. Such waters are not only unsuitable for irrigation, but cannot be used for other purposes. The flora and fauna of the rivers are endangered. The harmful effects of polluted river water directly or indirectly threaten humans.

In recent years, it has been established that different categories of pollutants enter the environment - chemical elements (Dehgashti et al. 2020), pharmaceutically active substances (Santos et al. 2021), pesticides (Ramakrishnan et al. 2021), pathogenic microorganisms (Núñez-Delgado et al. 2021), dyes (Tkaczyk et al. 2020), etc.

Pharmaceutically active compounds are complex molecules with different functions and physicochemical and biological properties. They are used due to their specific biological activity. Most of them are polar compounds. The molecular weights of the drugs typically range from 200 to 500/1000 Da. For this reason, they are also known as "small molecules." They are part of compounds called "micro-pollutants." These chemical molecules have been studied because of their presence, albeit in low concentrations ($\mu g/L$ or ng/L) in the environment (Fatta et al. 2007). They can remain in the environment (marine, estuaries, rivers, lakes, and underground water around the world) for a long time due to their continuous transport (Kuzmanovi´c et al. 2015). Their presence is considered dangerous at both lower (from ng/L to $\mu g/L$) and higher (mg/L) concentrations (Godwin et al. 2019). Even at these minimum concentrations, the presence of these medicinal compounds in water may pose a potential risk to aquatic and terrestrial organisms.

Pharmaceutical products found in soil, groundwater and wastewater (Farissi et al. 2022), drinking water (Kar et al. 2021), tap water (Mozia et al. 2012), sea water, sediment and soil (Durán-Álvarez et al. 2021), can be excreted (as active and inactive metabolites) from humans or animals by urine (Almuntashiri et al. 2021), feces, sewage system or treatment plants (Fawzi et al. 2021) (Fig. 1). All of them released into the environment can be toxic at almost any level in the biological hierarchy - cells, organs, organisms, populations, ecosystems, or the ecosphere. Metabolic excretion and disposal in agriculture and industry contribute to environmental pollution through manure, surface and groundwater (Khetan et al. 2007).
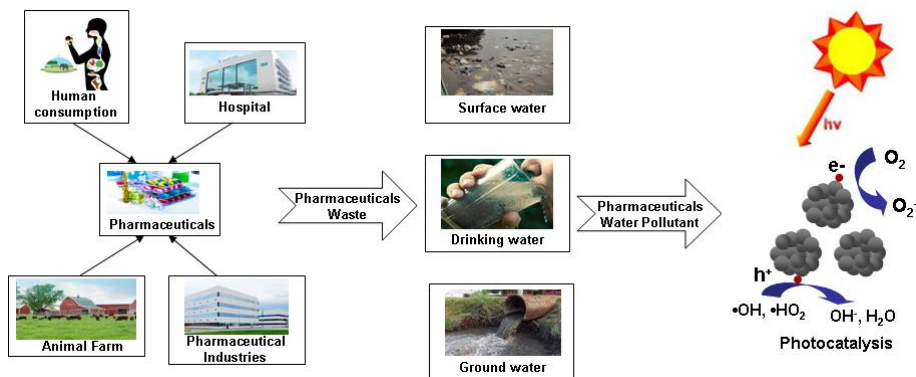
Figure 1. Possible methods of pharmaceutical entry to the environment

Pharmaceutical products degrade in aqueous media to: (i) compounds that mineralize to carbon dioxide and water, (ii) compounds that do not degrade easily because they are lipophilic and partially retained upon precipitation and (iii) compounds that are digested to a more hydrophilic molecule, which passes through the treatment plant and ends up in wastewater receivers (mainly rivers). These compounds show the highest resistance in the environment, due to their low concentration. More importantly, however, their presence in aqueous systems is dangerous, as these compounds disrupt the functions of the human endocrine system (Bredhult et al. 2007). The presence of residual drugs in the environment and aquatic systems is a serious environmental problem, as these compounds (i) are extremely resistant to biological degradation processes and usually remain unchanged by conventional treatment plants, (ii) can lead to serious toxic and other effects on humans and living organisms and (iii) are in low concentrations, thus requiring more complex methods for their elimination. Therefore, it is not surprising that recent research has focused on the application of non-biological processes for the destruction of pharmaceutical products in water by photocatalysis.

Heterogeneous photocatalysis belongs to the advanced oxidation processes (AOPs), which has been extensively explored and known as promising methods for removal of contaminants of emerging concern from wastewater effluents, for two reasons: (i) the variety of technologies developed and (ii) the wide range of potential applications.

AOPs include mainly: heterogeneous and homogeneous photocatalysis under the action of ultraviolet (UV) radiation or sunlight, photolysis; electrolysis; ozonation; oxidation by Fenton's reagent; ultrasound and oxidation with moist

air. Ionizing radiation, microwave radiation, or pulsating plasma is used in the conventional processes (Fig. 2), (Comninellis et al. 2008, Doll et al. 2003). AOPs are also used for wastewater treatment (Comninellis et al. 2008), groundwater, soil remediation, ultrapure water production, treatment of volatile organic compounds, and water odor control.
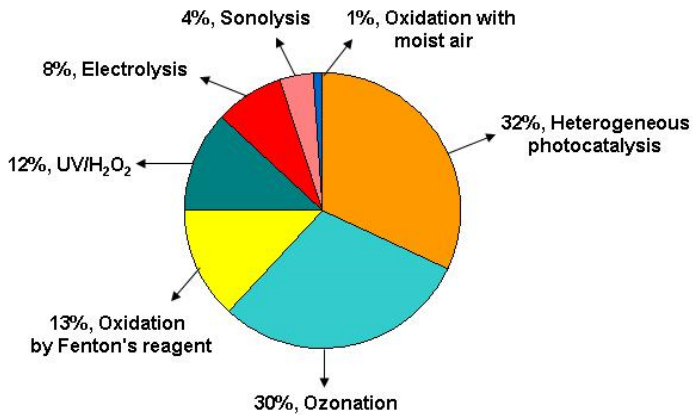

Figure 2. Different types of advanced oxidation processes for
the removal of organic pollutants

Heterogeneous photocatalysis has a number of advantages over the rest of oxidation processes: (i) takes place in environmental conditions, (ii) catalysts are cheap and commercially available, (iii) catalysts are characterized by different crystalline forms, which has an impact on the decomposition of organic pollutants, (iv) the catalysts are non-toxic and stable (Doll et al. 2003).

Heterogeneous photocatalysis uses metal oxide semiconductor nanostructures, such as ZnO (Weerathung et al. 2022), TiO_2 (Thambiliyagodage et al. 2021), WO_3 (Zhao et al. 2020), etc. All of them are able to purify water from chemical and biological contaminants in low concentrations. The successful photocatalyst must efficiently absorb light, preferably in the visible or near UV part of the absorption spectrum. When exposed to light (ultraviolet, visible, infrared, etc.) there must be enough vacant states, able to separate the electron-hole pairs of charges. The requirements for efficient photocatalyst are as follows: biologically and chemically inert, physicochemically stable, with high oxidizing ability at different temperatures and pressures, non-toxic, stable in the presence of electrolyte solutions, low price, large surface area in order to be used more efficiently in photocatalytic reactions.

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Methods for ZnO synthesis

The advantages of nanostructured ZnO as a photocatalyst (chemical stability, biological inertness, insolubility, reasonable price) have prompted the creation of a number of methods for its synthesis (Fig. 3). Different chemical and physical routes like solvothermal/hydrothermal, chemical precipitation, sol-gel, mechanochemical, microemulsion, and microwave methods for ZnO synthesis are reported in the literature.
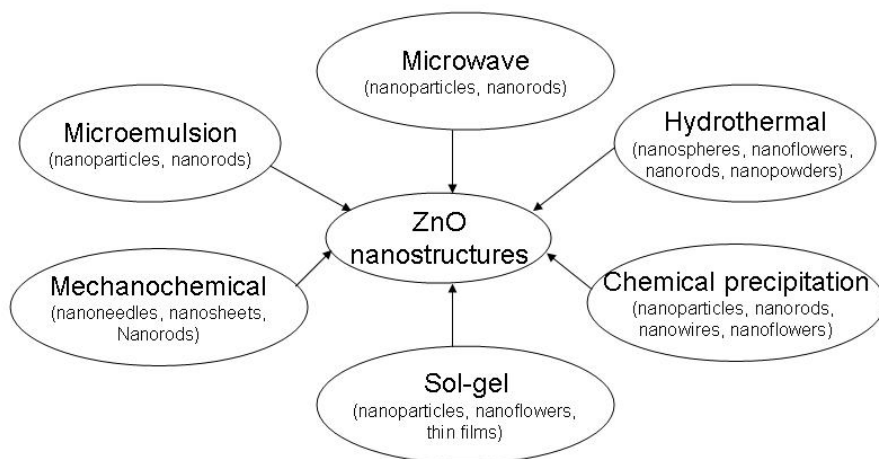

Figure 3. Synthesis methods for the preparation of ZnO nanostructures

The hydrothermal process has several advantages over other methods for obtaining nanostructured ZnO: simple synthesis technique, low temperature (60-100°C), high product yield, more controllable method, low cost and non-toxic reaction products - in order to protect the environment. This method is also successfully used for the production of nanosized ZnO and luminescent materials. The properties of the particles (morphology, size) can be controlled by regulating the reaction temperature, time and concentration of the precursors. In addition, ZnO obtained by this method has a crystalline phase, which is beneficial for its thermal stability (Wei et al. 2006).

Many authors around the world obtain nanostructured zinc oxide by hydrothermal method (powders, needles, rods, particles, etc.). Lu et al. (Lu et al. 2008) prepared core/shell type ZnO crystals consisting of sheet-like ZnO supported on pyramidal nanocrystals using ethylenediamine, treated at 160°C. This method is also suitable for modifying ZnO nanostructures in order to increase their photocatalytic activity in the presence of visible light.

The sol-gel method is a low consumable method for obtaining amorphous and polycrystalline thin layers with the desired morphology and thickness with a larger area. New valuable materials are obtained with wide applications. Bekkari et al. (Bekkari et al. 2017) used the sol-gel method and established the effect of the rate of addition of a precipitating agent on the morphology, crystallinity and nucleation rate of ZnO crystals. The crystallinity of ZnO nanoparticles decreased with an increase in the rate of NaOH (from 0.17 to 20 mL/min). On the other hand, the morphology of zinc oxide can be changed by studying the effects of sol aging (Kaneva et al. 2015). The sol is prepared by mixing zinc acetate dihydrate, 2-methoxy ethanol and monoethanolamine. The obtained solution is heated up at 60 $^{\circ}$C upon magnetic stirring for 1 hour. An aliquot is taken each 0, 30 and 60 days. Then, the thin films are deposited on the glass using the dip-coating technique (Fig. 4). These images show that there are changes in the morphology of the thin films with the sol aging time. The increase of the aging time of ZnO sol increases the volume and size of ganglia-like hills.
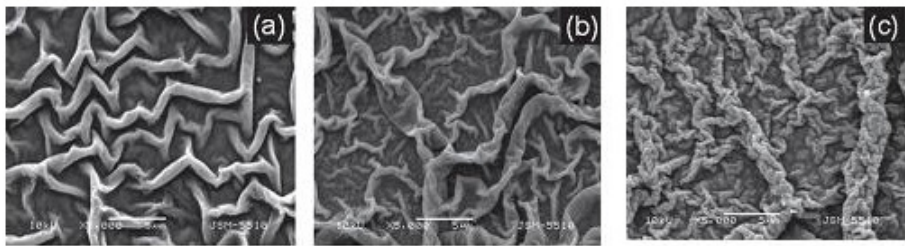

Figure 4. SEM images of ZnO films with five coats were obtained from sols aged (a) 0, (b) 30 and (c) 60 days

The mechanochemical method is used as an eco-friendly synthesis to obtain ZnO nanostructures by solid-state grinding (ball mill) of Zn precursors in the presence of a precipitating agent powder. Ao et al. (Ao et al. 2006) prepared ZnO nanocrystals by solid-state grinding of $ZnCl_2$, Na_2CO_3, and NaCl ($ZnCl_2$ to NaCl ratio = 8:1) using a ball-mill (600 rpm) for 6 h. In our previous work, we used mechanochemical activation (Kaneva et al. 2016). ZnO powders are treated in a high-energy planetary ball mill. The samples are mechanochemical activated for different milling time intervals 5 and 15 min at 400 rpm (milling speed) and the weight ratio 1:5 (sample and balls). The ZnO powders are treated for 20, 30, 40 and 60 min at 200 rpm and 1:3 mass ratio milling balls to powder. In this article the effect of solvents (methanol and ethanol) on the photocatalytic efficiency of zinc oxide is investigated. The commercial powders and the solvents are mixed and then they are mechanoactivated for 30 min at a milling speed of 200 rpm.

The microwave method has its advantages over others - single-phase particles, narrow particle size distribution, high crystallinity, fast reactions, rapid and uniform heating, and low energy consumption. This method is used to allow rapid and uniform heating for the hydrothermal reaction as compared to classical heating treatment. Microwave irradiation is the main factor affecting ZnO morphologies. The higher reaction rate and rapid growth of ZnO nuclei are observed with increasing of the microwave energy (Barreto et al. 2013). In our previous work, we synthesized thin films of sol-gel (Kaneva et al. 2015), and then thermally annealed them at 500°C for 1 hour. Now, these zinc oxide films instead of thermally activating them, we irradiated them with microwave energy (1200 W for 1 h). The experimental results show a more developed zinc oxide surface (Fig. 5) and better photocatalytic efficiency.
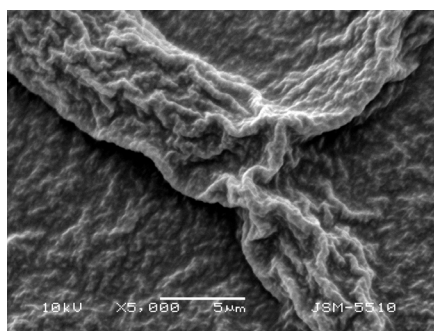

Figure 5. SEM image of ZnO sol-gel film after microwave treatment at 1200 W for 1 hour

Pharmaceutical drugs degradation using ZnO nanostructures

In the last few years, zinc oxide has attracted attention in the scientific community as a "material of the future". The main advantage of ZnO is its high exciton binding energy (60 meV), which is greater than the thermal energy at room temperature (Vaseem et al. 2010). The specific physicochemical, optoelectronic and magnetic properties of ZnO lead to its many potential applications in various fields, such as light-emitting diodes (Kim et al. 2011), solar cells (Sudhagar et al. 2011), gas sensors (Xu et al. 2008), photodetectors (Leung et al. 2010), etc. in addition to photocatalysis (Kaneva et al. 2015, Kaneva et al. 2016).

In general, the structural characteristics, including size, morphology, crystalline, have a significant influence on the properties of ZnO and are extremely important for its photocatalytic applications. Table 1 summarizes the experimental results of many authors using zinc oxide nanostructures to remove various drugs.

Table 1. Photocatalytic degradation of drugs using ZnO nanostructures

Pharmaceutical compounds	Degradation, %	Experimental conditions	ZnO nanostructures	References
Amoxicillin	100	[drug] = 104 mg/L pH = 8 UV lamp, 300 min	ZnO commercial, 0.5 g/L	Elmolla et al. 2010
Ampicillin	100	[drug] = 105 mg/L pH = 11		
Ciprofloxacin	50	[drug] = 5 mg/L Xenon lamp, 60 min pH=10	ZnO (precipitation) 0.02 g/L	El-Kemary et al. 2010
Ciprofloxacin	90	[drug] = 10 mg/L Hg lamp, 140 min pH= 5	ZnO 0.15 g/L	Eskandari et al. 2018
Diclofenac	68	Hg lamp, 30 min [drug] = 1 mg/L pH = 7	ZnO commercial 0.05 g/L	Bohdziewicz et al. 2016
Ibuprofen	59 / 36	[drug] = 5 ppm UV–vis solarium lamps, 180 min (60 W)	Synthesized nano ZnOw (solvent water), ZnOe (solvent etanol) 0.02 g/L	Choina et al. 2015
Paracetamol	63	[drug] = 15 ppm UV lamp (18 W) 240 min	ZnO sol-gel, thin film	Kaneva et al. 2015
Chloramphenicol	45	[drug] = 8 ppm		
Paracetamol	40	[drug] = 15 ppm UV lamp (18 W) 240 min	ZnO nanowires	Kaneva et al. 2013
Chloramphenicol	3	[drug] = 8 ppm		
Paracetamol	96	[drug] = 15 ppm UV lamp (18 W) 240 min	ZnO commercial 0.5 g/L	Kaneva et al. 2016
Chloramphenicol	95	[drug] = 8 ppm		
Carbofuran	90	[drug] = 200 mg/L Hg lamp, 360 min pH= 7	ZnO commercial 1 g/L	Mahalashmi et al. 2007

Discussion on the efficiency of zinc oxide catalysts

The removal of contaminants by heterogeneous photocatalysis increases with increasing ZnO concentration. Increasing the catalyst concentration provides a larger number of active sites and therefore a higher generation of electron holes. This causes the increased formation of hydroxyl and superoxide radicals, which facilitate the decomposition of pollutants in the environment. On the other hand, the high concentration of photocatalyst can causes agglomeration of the particles, thus reducing the presence of active sites, respectively the efficiency of decomposition of pollutants. For these reasons, the optimal catalyst concentration

must be used. The concentration of drugs is an important factor that affects the activity and kinetics of degradation, as well as the optimal dosage of the catalyst (Mahalashmi et al. 2007).

The high concentrations cause the deactivation of the photocatalyst. Mahalakshmi et al. (Mahalashmi et al. 2007) reported that the optimum concentration of ZnO for the mineralization of 200 mg/L Carbofuran is 1 g/L. This effect has also been studied by Choina et al. (Choina et al. 2015). They found experimentally that increasing the concentration of the pollutant from 5 to 60 ppm, this leads to a decrease in the efficiency of the catalyst (from 65% to 5% after 180 minutes of irradiation).

Kemary et al. (El-Kemary et al. 2010) obtained ZnO nanostructures by chemical precipitation method for the mineralization of Ciprofloxacin. It has been studied in detail photocatalytic degradation of the drug at different pH of the reaction medium (ranging from 4 to 10). It is known that the pH of the reaction medium is an important parameter for properties of the photocatalyst and rupture of bonds in the chemical structure of the drug. The faster mineralization of Ciprofloxacin at neutral and alkaline pH is due to the formation of hydroxyl ions, which are converted into radicals by interacting with the holes in the valence band of zinc oxide. Hydroxyl radicals have a high oxidative potential, thus increasing the degradation process of the drug. The reason for the low degree of mineralization in an acidic environment is due to the delay of formation of protons in high concentration and the dissolution of ZnO photocatalyst. Eskandari et al. (Eskandari et al. 2018) also reported similar results (Table 1). Similar to these results (related to the concentration of zinc oxide and the pH of the solvent), many authors have found experimentally and other effects - light source, irradiation time, temperature, which affect the photocatalytic degradation of various drugs (Table 1).

In our previous articles, we used different methods for the obtained of zinc oxide materials – nanowires (Fig. 6a, Kaneva et al. 2013), sol-gel thin films thermally activated (Fig. 6b, Kaneva et al. 2015), commercial powder thermally (Fig. 6c, Kaneva et al. 2016) and mechachemically activated (Fig. 6d, Kaneva et al. 2016). All these nanostructures are used for the photocatalytic degradation of two drugs - Paracetamol (PCA, analgesic) and Chloramphenicol (CA, antibiotic) by UV-vis spectroscopy. The degradation of drugs follows pseudo first-order kinetics according to the Langmuir-Hinshelwood model. The values of rate constants (k) are calculated from the corresponding $\ln(C/C_0)$ versus irradiation time, using this equation $\ln(C/C_0) = -kt$, where C_0 is the initial drug concentration, while C is the drug concentration at the moment t of the process.
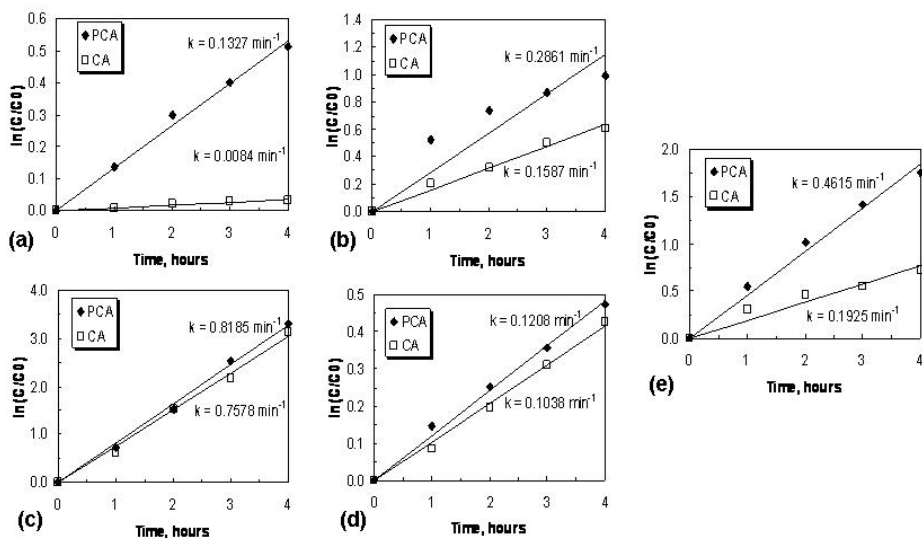
Figure 6. Kinetics of PCA and CA drugs degradation under UV-light illumination using different ZnO nanostructures: (a) nanowires, (b) sol-gel thin film thermal activated, (c) commercial powder thermal activated, (d) commercial powder mechanochemical treatment, (e) sol-gel thin film microwave activated.

From Fig. 6, it is clear that zinc oxide nanowires most slowly degrade drugs. The values K of their rate constants show their lowest photocatalytic activity. Respectively, zinc oxide commercial powder (annealed at $500^{\circ}C$ for 1 hour) has the highest efficiency and fastest degradation of the drugs.

In this review, we prepared for the first time ZnO thin films treated with microwave irradiation and investigated their photocatalytic properties for the degradation of pharmaceutical products. In this review, we compared the two types of photocatalysts - thermally and microwave activation. The degradation efficiency over ZnO thin film thermal activated ($k_{PCA} = 0.2861$ min^{-1}, $k_{CA} = 0.1587$ min^{-1}) is lower in comparison with ZnO thin film microwave treatment ($k_{PCA} = 0.4615$ min^{-1}, $k_{CA} = 0.1925$ min^{-1}). The reason for this result is not clear and is probably due to various factors – the size of crystallite, the width of the diffraction peaks. Microwave activation has its advantages rapid and uniform heating, and low energy consumption.

CONCLUSION

Heterogeneous photocatalysis is a promising method for removing emerging pollutants in wastewater. Among semiconductors, ZnO is cost-effective, easy to manufacture and can absorb a wide range of light spectrum at the threshold of 425 nm. The effect of the morphology and structure of different ZnO nanostructures is considered and summarized in this review. Different forms of ZnO show promising photocatalytic properties against various pharmaceutical drugs in wastewater. However, several parameters such as catalyst dosage, substrate concentration and pH need to be considered and optimized for an effective removal process. Literature studies show that the formation of by-products during the photocatalytic decomposition of emerging contaminants with ZnO is negligible. On the other hand, the by-products formed may be more toxic than the starting compounds, then their removal is essential. The following conclusions can be drawn from this literature review:

- The uncontrolled release of pharmaceutical drugs into the environment is dangerous to human health as well as to other living species. Therefore, the degradation of complex drug structures into simple inorganic compounds is imperative;
- Heterogeneous photocatalysis, using different ZnO nanostructures, shows that it can solve existing water problems due to contamination with pharmaceutical drugs;
- Parameters, such as pH of the medium, nature of the solvent, operating temperature, etc., play an important role and affect the overall efficiency of the photocatalyst. pH controls the dissociation, solubility, polarity of pollutants, and the potential dissociation of catalysts;
- Pharmaceutical compounds are found in high concentrations (ppb or ppt) in wastewater. For this reason, further tests are needed to determine the presence of traces of contaminants in wastewater from treatment plants. It is imperative to identify by-products as well as photocatalysis intermediates to ensure that the products formed are not harmful to the environment.

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