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# EPs Antibiotics: Photodecomposition and Biocarbon Adsorption

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## Abstract

The emerging pollutants (EPs) are considered a global monitoring challenge, present in the environment in very reduced concentrations, and the proper methods for sampling and analysis are still in development. Many published types of research considering the EPs identification only depend on the analytical methodology and a more efficient higher number of EPs. The quantitative determination of the prioritized EPs in water needs advanced and ultra-sensitive instrumental techniques applied in water, water-suspended matter, soil, and biota. The regulatory framework of the water-quality parameters does not often include the microplastics, EPs, and their metabolites; especially, the ground-water water-quality monitoring and control are urgent but not yet achieved. The EPs sources in water are the sewage, industrial, and agricultural waste discard, and the UN estimated that the wastewater produced annually is about 1500 km<sup>3</sup>, about six times more water than existing in all rivers of the world. In 2015, in China, which has a fast-growing economy, the water is a scarce resource with just 8% of the world's fresh water to meet the water needs of the 22% of the world's population.

**Keywords:** emerging pollutants, biocarbon, biochar, antibiotics, solar, photodecomposition

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## 1. Introduction

In the world, about 33% of the industrial wastewater and 70% of the household sewage are untreated and directly discharged into rivers and lakes, while 80% of China cities have no sewage treatment facilities and water supplies in 90% of the cities, the water being contaminated [1]. There are 20 classes of categorized EPs accordingly with their origin; the prominent categories are pharmaceuticals (urban and protein production), pesticides (agriculture), disinfection

by-products (urban and industry), wood preservation, and industrial chemical manufacturing. Different types of EPs show different properties as the organic substances divided in PBT for persistent bioaccumulative and toxic substances as POPs and persistent organic compounds. The EPs with more polarity are the pesticides, pharmaceuticals, and industrial chemicals. The inorganic compounds as poisonous metals are also found in polluted waters and finally the newly developed particulate contaminants as nanoparticles and microplastics [2].

The EPs monitoring and control are a huge problem, and the solution represents a significant challenge in sampling procedures and analytical techniques. The monitoring procedures do not cover all EPs with a potential concern being the highly known hazardous controlled, and the newly discovered contaminants as nanomaterials and microplastics are virtually analytically nonexistent. In the study, the EPs presence and toxicity are studied using bioindication; the most common organism is the *Gammarus pulex* as a model invertebrate from water and sediment.

The properties such as absorption behaviors of pharmaceuticals, for example, can vary vastly in different soil types on ionized and nonionized form, affecting the interaction of soil. Little information is available about the EPs dynamics in the water column, sediments, and the accumulation in the aquatic food chain and the loads from the agro-environment through diffuse pollution or from urban and industrial areas [3, 4].

The EPs decomposition products detection includes enantiomeric distribution of chiral compounds found in the environment, and their possible toxicological differences between enantiomers that are of concern. Such information for the risk assessment analysis is also considered [3].

Worldwide, the regulatory framework is under development to control the production and the discharge of the EPs into water resources, a complex set of regulations governing the production, commercialization, and emission to control the EPs presence in the environment and the drinking water (quality standards and monitoring specification). The European Union (EU) has a regulation plan to register, evaluate, authorize, and restrict the use of almost all EPs substances manufactured or imported to EU.

The agricultural activity is one of the most critical contributors to diffuse pollution in Europe, and such emissions are predicted to increase in the future. The agriculture activity is considered an essential business for regulating the chemical EPs use and emission discharge into the environment. Some research projects are under development, trying to treat, decompose, and remove those pollutants from the water resources.

The emerging pollutants are considered the potentially toxic chemicals present in low concentrations and many environmental compartments. They include pesticides, biocides, pharmaceuticals, industrial chemicals, and personal care products. The common entrance of these compounds in surface water resources is via untreated sewage discharge, the effluents of wastewater treatment plants (WWTPs), and from agricultural, urban, and street runoff. The organic pollutant water inputs usually occur continuously in low dosages or as peaks triggered by emission or runoff events. Such a behavior is particularly harmful to antibiotics environmental contamination, providing the optimized conditions for microorganism adaptation and increase in resistance.

The concept of chemical activity helps to understand the EPs environmental fate, distribution, quantification, and prediction of the ecological partitioning theory of the chemicals in aquatic

systems as water column, sediment (mostly organic matter), and biota (lipids and proteins). It addresses single compound or mixtures reaching the equilibrium. The chemical activity relies on partition coefficients which are only available as experimental values. There are some models calculating partition coefficients from octanol–water systems (Kow-based models), and they were used for decades to estimate the concentration in different compartments.

Nowadays, the relationship of the polyparameters linear-free energy is used to calculate the partition coefficients of biological and nonbiological matrices including lipids and different proteins [4, 5]. The model helps to describe the diffusion and partitioning processes and estimate when an environmental compartment acts as an EPs source or a sink for a single contaminant or a multi-compartment system.

## 2. EPs photodecomposition

Two of the main topics of growing concern in analytical chemistry are the development of green water treatment.  $\text{TiO}_2$  has emerged as a promising photocatalyst for environmental cleanup applications; they have efficiently decomposed and removed a variety of pollutants promoting the generation of OH radicals using oxidation reactions with in situ active oxygen generated upon light irradiation. In water purification, photodegradation of contaminants in real water samples has become an important topic of research in the recent years.

There are some studies using electrocoagulation process to decompose EPs compounds. The process is an electrochemical introducing coagulants and removing suspended solids, colloidal material, and metals as well as other dissolved solids from water and wastewater eliminating pollutants, pesticides, and radionuclides. A direct current is applied, and one electrode is soluble into a solution which finally precipitates as oxides or hydroxides.

The environmental chemistry is the base for many treatment technologies of these pollutants, and the application of the adsorption process is one of the most used techniques. The results and comparison of different treatment technologies usually consider the initial concentration and the final concentration. The adsorbent materials are graphene oxide, clay mineral and biochar, nanocrystalline mineral, and arsenite using an enhanced coagulation process [6, 7]. The pharmaceuticals used iron chemical reduction reaction, and the advanced oxidation performed by ozone/UV also was used. The pharmaceuticals uses iron chemical reduction reaction, and the advanced oxidation performed by ozone /UV. The study of micropollutants biodegradation uses also a membrane.

The most common material used for EPs adsorption is the activated carbon (AC) with high porosity and surface area, and the use of AC shows the removal percentage higher than 90% for a wide variety of compounds bringing the residual concentration below the regulation limit. Other materials need more contact time for the same results. The advanced wastewater reclamation plant often uses the AC [5]. Many authors point out the high importance of the AC origin, depending on the initial crystalline structure of the biomass, the AC obtained from wood, vine, and olive waste, and coal showed the removal percentage always higher than 80% for antibiotics.

There are some adsorbents used for pharmaceutical removal as biochar, clay minerals, zeolites, Fe-Mn-binary oxide, graphene oxide, alumina, nanoscale iron, molecularly imprinted polymer, and carbon nanotubes [5, 8].

The phase extraction uses organic phase to remove organic contaminants, and the use of membrane technology is for pharmaceuticals removal from polluted waters. The bases of the membrane technology are the hydrostatic pressure to remove suspended solids, and solutes with a high molecular weight also classified as ultrafiltration, nanofiltration, microfiltration, forward osmosis, and reverse osmosis. The high removal percentages are obtained for forward and reverse osmosis with the removal percentages usually more than 95%.

The biological processes in conventional activated sludge decompose only the natural pharmaceutical compounds like caffeine, dichlorofenac, and trimethoprim. The advanced oxidation processes provide higher removal percentages associated with the hydroxyl radical production with removal percentages always higher than 96% including the sonochemical decomposition. The solar photo Fenton process obtains the removal percentage of 95–97.5% in just 20 min of reaction.

Many published results indicate that the degradation of EPs using a single treatment is not likely the best approach to treat and remove EPs from water, and the use of a combined technology can overcome deficiencies of individual technologies and be able to ply in complex mixtures of contaminants. The advanced oxidation processes are at present the most efficient degradation processed for EPs contamination.

The results of the kinetics studies of photodecomposition and biocarbon sorption provide valuable insights about the kinetics models: pseudo-first-order (Eq. (1)), pseudo-second-order (Eq. (2)), and intraparticle (Eq. (3)) with the determination of photodecomposition and adsorption rates on pseudo-first-order equation [9, 10].

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (1)$$

where  $K_1$  is the pseudo-first-order rate ( $\text{min}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ ) refers to the experimental adsorbed mass at equilibrium. The plotting of the calculated values of  $\ln(q_e - q_t)$  for  $t$  (time) and the calculation of  $K_1$  were used the slope values of the line equation.

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{K_2} + \frac{1}{q_e} t \quad (2)$$

where  $K_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) is the kinetics adsorption rate, plotting the  $t/q_t$  for  $t$  (min), and the calculation predicted the adsorption capacity  $q_e$  ( $\text{mg g}^{-1}$ ) and the integrated adsorption rate  $K_2$  with the slope and the intercept of the line equation, respectively.

Intraparticle equation:

$$\log(q_t) = \log(K_{id}) + \log(t) \quad (3)$$

The use of the experimental results allows performing the kinetics calculations [11–13], using Eqs. (1)–(3). The pseudo-first-order equation represents a logarithm of the reactant species



and the reaction time; larger  $K_1$  indicates a fast reactant consumption and small time to complete the reaction; the  $R^2$  values obtained for the pseudo-first equation indicate a lower correspondence between the results and the theory. Some published results show the solar photodecomposition processes with goethite as pseudo-first-order kinetics with  $K = 0.26 \times 10^{-2} \text{ min}^{-1}$ . Usually, the photodecomposition experimental results indicated a lower correlation with pseudo-first-order, sometimes just one  $K_1$  value; all results showed a better correspondence with the pseudo-second order.

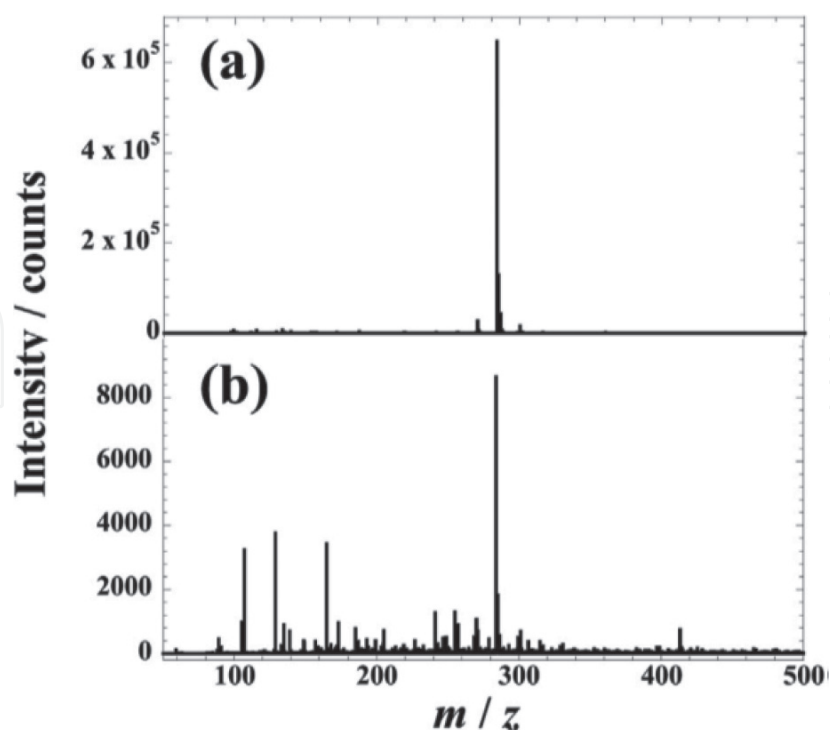
Considering the pseudo-second-order reaction, the sum of the exponents in the equation rate is equal to two for the plotted reactant concentrations with time. The pseudo-second-order response depends on the initial content, of the two different reactants A and B combining in a single elementary step. Before the rate, where A decreases, they can be expressed using the differential equation, and the linear equation can be rearranged, integrated, and followed where the slope value is  $K_2$ . The pseudo-second order showed better correspondence with the experimental results corroborating with many published results for biocarbon adsorption and amoxicillin (AMX) removal treatments. The interparticle reaction usually points out the slow step of the adsorption reaction.

The use of integrated processes as solar/ $\text{TiO}_2$  photodecomposition followed by adsorption has many advantages as an excellent potential for photocatalysis with the application of solar treatment chambers and possible self-cleaning surfaces. However, the practical applications and continuous use demand solutions to kinetics problems, and they may rise as the adsorbent-reduced surface area,  $\text{TiO}_2$  oxidation surface, and solid low stability due to long-term use and the potential oxide mass production. The amoxicillin degradation with solar/ $\text{TiO}_2$  anatase proceeds about three times faster than with ultraviolet (UV) lamp [14, 15]. The explanation of the disproportional improvement oxidation rates is the difference between the small spectrum irradiance of UV band and the broad spectrum of visible solar light. The intensity of radiation spectrum grows with an increasing wavelength from 300 to 500 nm. The combination of solar photodecomposition and the adsorption process is efficient and low cost.

### 3. The antibiotics photodecomposition products

The electrospray ionization mass spectrometry (ESI-MS) analytical technique measures the EPs methylene blue (MB) photodecomposition. Before the photodecomposition reaction, the methylene blue compound was  $m/z$  284 (**Figure 1(a)**), and after 1 day of photodecomposition, there are several peaks (**Figure 1(b)**). Those peaks were MB fragment degradation compounds with  $m/z$  values of 109, 129, and 165. Those peaks have the relative intensity of 37.3, 44.2, and 40.5% considering the original MB peak of 100% with  $m/z$  284 (**Figure 1(a)**).

The EPs dye photosensitization process involves the dye initial electronic excitation  $D$  to  $D^*$  induced by  $h\nu$  incident radiation energy which ejects one electron in the semiconductor (SC) conduction band [8, 16, 17]. The emitted electron reacts with the environment oxygen oxidizing the radical  $D^{\bullet}$ , and the total process results in colorless products, Eq. (6).



**Figure 1.** ESI-MS spectra of methylene blue photodecomposition (a) before and (b) after degradation of 1 day (adapted from Kobzi et al. [27]) [8].

The study provides some example of dye sensitization, and the photosensitized bleaching occurring under visible light and an aerated aqueous dispersion of  $\text{TiO}_2$ . The light absorbed by the dye alone was able to promote its rapid and complete photobleaching. The photonic efficiency  $\eta$  for the visible photobleaching of the MB is already known, and it is a function of the incident radiation wavelength. The spectrum  $\eta$  versus  $\lambda$  plot was similar in shape to the diffuse reflectance spectrum (DRS) of the MB adsorbed on  $\text{TiO}_2$  with a peak at 665 nm which is the wavelength of the maximum adsorption for MB.

By contrast, the dye photolysis involves the electronically excited state of the dye which is either unstable and quenched by ambient  $\text{O}_2$  to produce singlet oxygen which oxidizes the dye. Considering only the equation, it is not surprising if the rate of dye bleaching due to photolysis is often unchanged in the absence of the semiconductor. When the photolysis and photosensitization are examined, the presence of SC enhances the production of the bleached product.



The rapid and irreversible reduction of the photogenerated holes by glycerol followed the reduction reaction and the molar absorptivity of  $4.7000 \text{ M}^{-1} \text{ cm}^{-1}$  at 620 nm. The glycerol behaves as an SED which is also present in the ink film. The MB photocatalytic process runs as follows:

The use of photocatalyst indicator (paiis) helps to measure the electron generation efficiency of the  $\text{TiO}_2$ , changing from blue redox dye Resazurin (Rz) to pink Resorufin (Rf). The Rz as

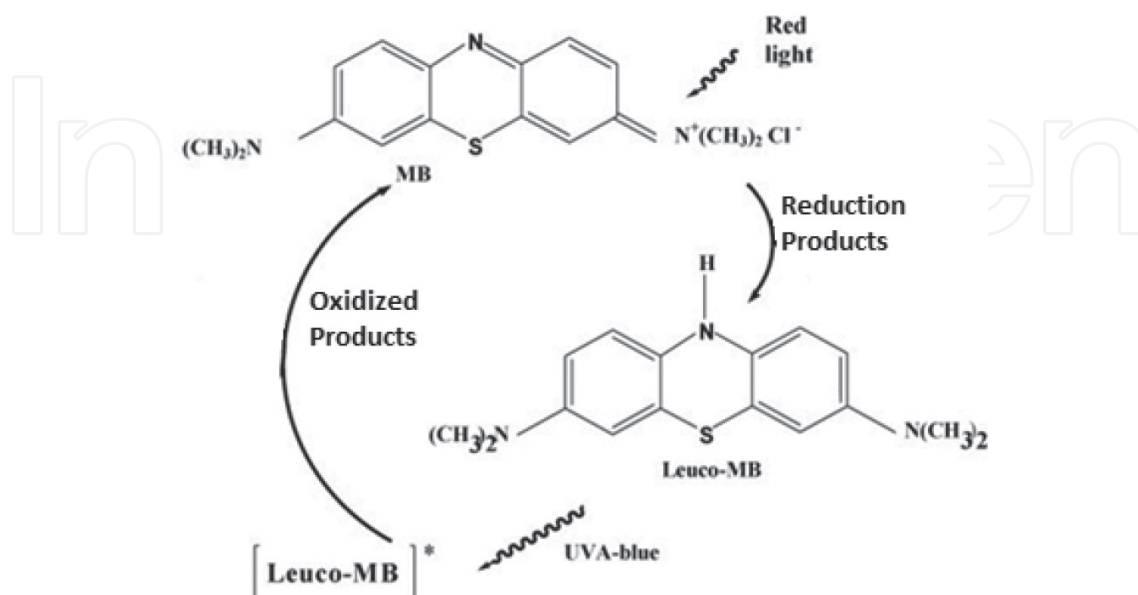
the MB adsorbs little in the UVA region. The elimination of the photogenerated holes by the glycerol, which acts as an SED, followed the reduction reaction.

Photocatalyzed MB redox reaction:



The colorless species identified as Leuco methylene blue (LMB) is readily re-oxidized to MB by ambient  $\text{O}_2$  and has to be produced and maintained in anaerobic conditions to be stable, **Figure 2**. This environmental condition also ensures that the traditional dye-sensitized bleaching reaction cannot occur [19, 20].

The MB is excited under the red region of the light source and received electrons to the excited MB which produces an anion which abstracts a proton from water to provide LMB; the LMB is very readily re-oxidized back to MB if there is any oxygen in the solution [9, 10, 21]. The CG results showed no change in the MB concentration for the first few minutes of reaction, but if the reaction progresses, efficiently all molecules of MB will be converted to LMB. Subsequently, the visual observation indicates that the intense blue color of the solution starts to disappear as the reaction progresses as an effect of the photoreduction of the MB to LMB at the adsorption band of MB. Experimental results indicated the irradiation of the MB at 365 nm in the absence, and the presence of glycerol electron donor occurs, and the MB rapidly photobleached via an oxidative route with LMB primary production in 15 min. The air presence also quickly reduced the LMB to MB, gaining 92% of the original color.



**Figure 2.** Scheme for photodecomposition mechanism of MB and the Leuco MB (LMB) production [9, 10].

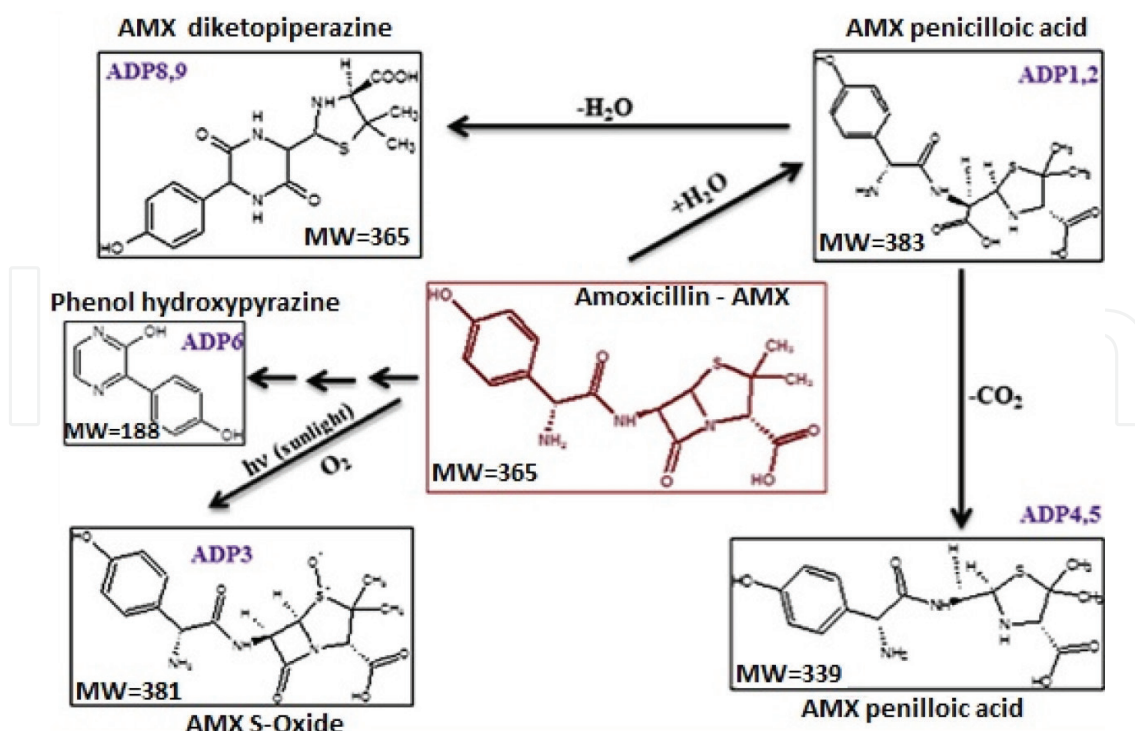


The photocatalytic dye bleaching process using the  $\lambda = 617$  nm is much slower than the reaction mediated by  $\text{TiO}_2$  and  $\lambda = 365$  nm light. The MB/glycerol has the potential as the dye-based test for UV presence, and visible absorbing photocatalytic materials provided by photocatalyst test.

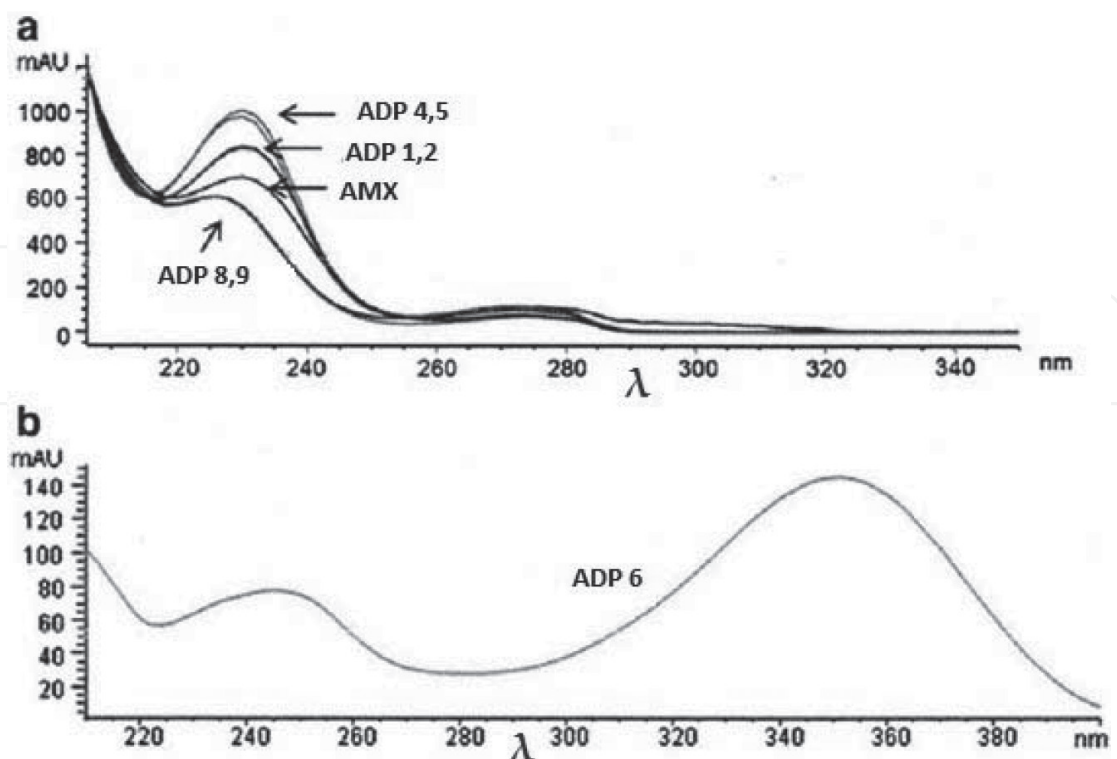
The redox potential for the reduction of MB at pH 7 to LMB is 0.011 v, whereas for oxygen it depends on electron transference and how many are present. For  $4e^-$ ,  $\text{O}_2/\text{H}_2\text{O}$  (0.815 v) and for 1 electron  $\text{O}_2/\text{O}_2^-$  (-0.33 v). It is not obvious that an SC is capable of reducing MB to LMB and also will be able to reduce  $\text{O}_2$ . The oxi-reduction indicator dyes are important to visualize the redox chemistry and measure the dye environmental oxidation/reduction.

The environmental antibiotics resistance to widely used medical and veterinary medicine is a serious problem and poses a significant threat to the health of humans and livestock infected with resistant bacterial strains. The alarming fact is that resistant genes can be mobilized between various environmental compartments and transferred into the food chain. The conventional processes associated with sewage treatment, hydrolysis, biodegradation, and sorption are ineffective for the removal of many antibiotics, and thus the photodegradation may be the predominant transformation pathway for antibiotics deactivation in the environment.

The UV spectra of amoxicillin (AMX) and the amoxicillin decomposition products (ADPs) as ADP1,2, ADP4,5, and ADP8,9 consisted of two peaks at  $\lambda = 230$  and 275 nm, similar with AMX. This effect is due to the para-substituted phenolic group, which do not change in the AMX and ADPs skeleton (**Figures 3 and 4**) and is the primary contributor to the observed UV spectra. Those peaks enable a quantitative calculation of these ADPs in the environment based on the assumption that the UV RF is relatively similar for AMX and its ADPs at  $\lambda = 230$  nm.



**Figure 3.** Suggested photodegradation pathway of amoxicillin in an aqueous medium (adapted from Gozlan et al., 2010) [7].



**Figure 4.** UV spectra of (a) amoxicillin and degradation products ADP1,2, ADP4,5, and ADP8,9 and (b) the degradation product ADP6 [11].

On the other hand, the compound ADP6 has conjugated double bonds (**Figure 3**), and thus, its UV spectrum consists of two different peaks at  $\lambda = 240$  and  $250$  nm. The calculation and quantification of ADP could not be in the environment due to the incompatibility of the AMX and ADP6 UV spectrum at  $\lambda = 230$  nm.

The confirmation of the proposed AMX DP structures was by comparison of the  $^1\text{H}$  NMR spectra of the AMX and those of purified ADP. **Figure 4** presents the degradation schematics of the AMX to its ADPs, the products ADP1,2, ADP4,5, and ADP8,9 are epimers, and preparative purification was carried out separately for each.

The penicilloic acid epimers (ADP4,5) are rapidly isomerized and become stable at an isomer ratio of 3:2, so the NMR spectra could not be obtained separately, **Table 1**. The isomers spectrum showed that H in the AMX spectrum is  $\delta = 5.44$  ppm, consisting of two hydrogen atoms, which shift to a higher field and become H-6a and H6b  $\delta = 5.18$  and  $4.46$  ppm, the ADP3 and ADP 8,9.

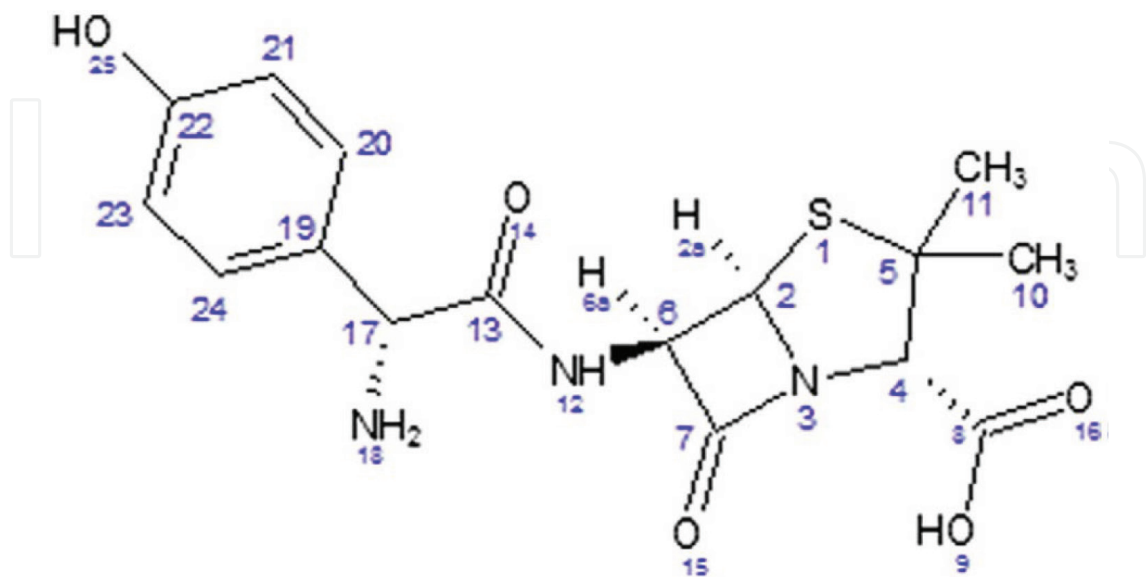
In recent years, the water-quality monitoring results indicated the presence of antibiotics and antibiotics residues in aquatic environments in many countries, including Europe, North America, and Asia. In addition, the antibiotic-resistant bacteria have become a serious problem worldwide, caused by the excessive use and incorrect discharge of antibiotics into the environment.

The use of ampicillin (AMP) is worldwide, as an essential antibiotic but this organic molecule rapidly decomposes in water containing bivalent cations as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and their

| Hydrogen        | AMX  | ADP1 | ADP2 | ADP3 | ADP4 | ADP5 | ADP6 | ADP7 | ADP8 |
|-----------------|------|------|------|------|------|------|------|------|------|
| CH <sub>3</sub> | 136  | 0.95 | 1.33 | 1.20 | 1.37 | 1.26 |      | 131  | 1.28 |
|                 | 1.37 | 1.53 | 1.39 | 1.57 | 1.53 | 1.62 |      | 1.65 | 1.66 |
| H-4             | 4.09 | 3.97 | 3.67 | 4.31 | 4.00 | 4.09 |      | 3.69 | 3.69 |
| H-17            | 5.07 | 5.18 | 5.10 | 4.99 | 5.09 | 5.09 |      | 4.91 | 4.95 |
| H-2             | 5.44 | 5.17 | 5.37 | 5.25 | 4.95 | 5.05 |      | 5.17 | 5.15 |
| H-6a            | 5.44 | 5.18 | 4.46 | 5.90 | 3.54 | 3.70 |      | 3.90 | 4.39 |
| H-6b            |      |      |      |      | 3.87 | 3.83 |      |      |      |
| H-21,23         | 6.92 | 6.96 | 6.96 | 6.94 | 6.96 | 6.96 | 6.81 | 6.82 | 6.82 |
| H-20,24         | 7.31 | 7.40 | 7.40 | 7.31 | 7.35 | 7.35 | 8.13 | 7.18 | 7.18 |
| ADP6            |      |      |      |      |      |      | 7.24 |      |      |
| ADP6            |      |      |      |      |      |      | 7.45 |      |      |

**Table 1.** The RMN results for amoxicillin photodecomposition and byproducts [11].

detection in the environment is difficult. The development of analytical technique allows the identification and quantification of the ampicillin and ampicillin degradation by-products as 2-hydroxy-3-phenylpyrazine (HPP) in the environment. The results indicate their presence in 42–79% of the monitored rivers and household ponds but they were not detected in aquaculture ponds. In these locations, the HPP concentrations were in the range of 1.3–413.3 ngL<sup>-1</sup>.The research results indicate the HPP presence as a promising marker for AMP presence and other β-lactam antibiotics with AMP substructure into the environment [22, 24, 25] (Figures 5 and 6).



**Figure 5.** Amoxicillin chemical structure.

The  $\beta$ -lactams antibiotics such as ampicillin, penicillins, cephalosporins, and oxicephalosporins inhibit biosynthesis of the bacterial cell wall by acylating and thereby inactivating transpeptidases. The antibacterial activity depends on the  $\beta$ -lactams rings, and some complex

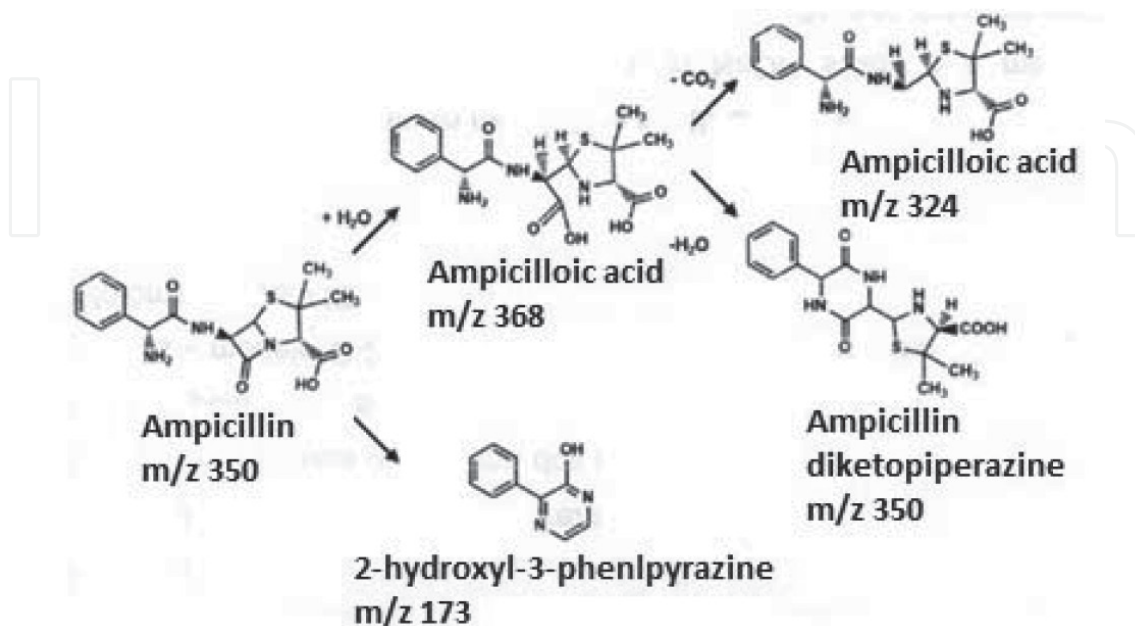


Figure 6. The photodecomposition scheme for ampicillin and its by-products.

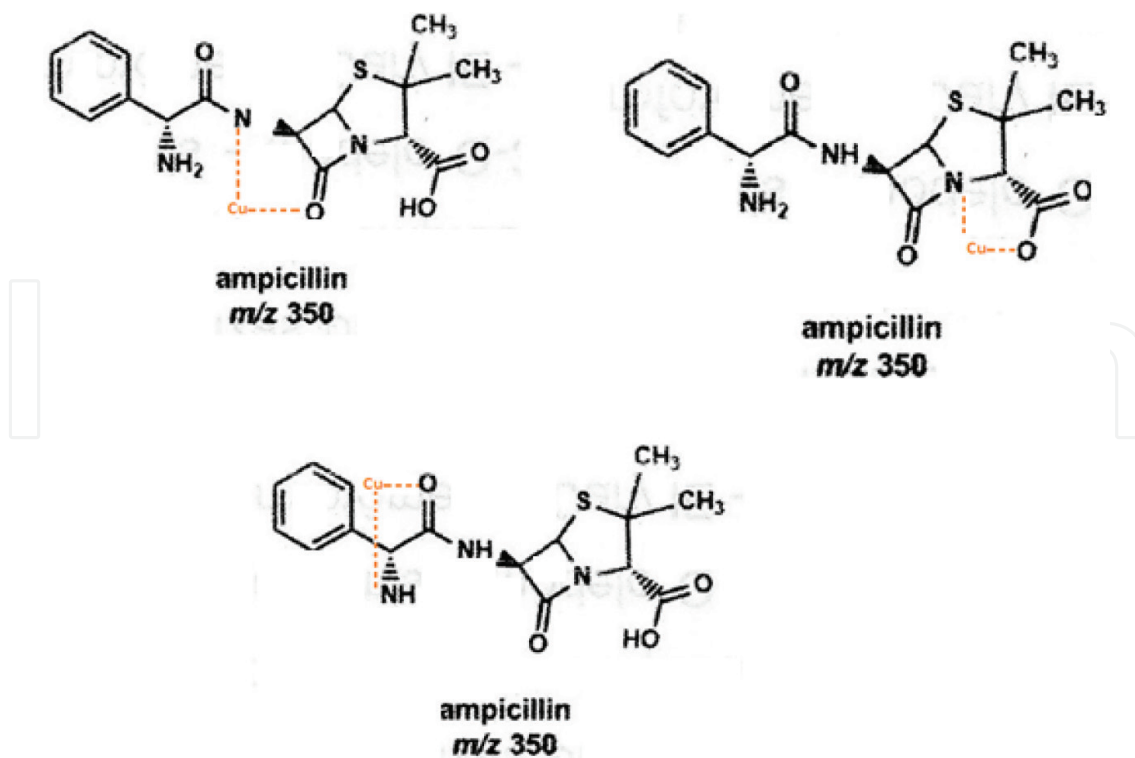


Figure 7. The complex formation with Cu-ampicillin chemical structure as a complex ligand.

compounds are responsible for their deactivation. There are several possible sites of the coordination for the metal ions on penicillin. The nitrogen and the double oxygen bonding are the most probable [13, 24, 26].

The amoxicillin and many antibiotics can act as a complex ligand with several possible sites for metal ions like Cu (II), Zn (II), and Cd(II) for coordination on penicillin. In the study, the kinetics and thermodynamics calculations are easy to find and how the neighboring group affects the probable complexation sites, of metals and the C=O of the antibiotic  $\beta$ -lactamic group and the NH amido penicillin group. The two most probable structures are shown in **Figure 7**. They are not excluding each other. For cephalexin and  $\text{Cu}^{2+}$ , the interaction takes place through the side chain, the same as expected for ampicillin structure.

The metal ligand binary constants at temperature  $37^\circ\text{C}$  and ionic strength for ampicillin and  $\text{Co}^{2+}$  are = 3.12, for  $\text{Ni}^{2+}$  = 3.66, for  $\text{Cu}^{2+}$  = 4.79 and for  $\text{Zn}^{2+}$  = 2.98. Usually, the complex constants with Cooper are more stable [14, 23].

#### 4. Binary and ternary antibiotics mixture

The  $\text{TiO}_2$  is steady, inexpensive photocatalyst, and widely applied for removal and decompose organic pollutants. However, the poor selectivity of the  $\text{TiO}_2$  is not conducive to remove high toxic contaminants from mixed solution, mostly in the presence of other pollutants [15, 16]. Some studies use tetracycline (TC) as a molecular template and the  $\text{TiO}_2$  fly ash cenospheres as a supporter, the synthesis of the molecularly imprinted photocatalyst (MIP). Such a material possesses the specific recognition ability toward tetracycline (TC) using surface-imprinting technology and the photo-induced method. The cenospheres hollow spherical structure has the diameter from 90 to 120  $\mu\text{m}$ , and the degradation process of photocatalytic activity of MIP with  $20 \text{ mgL}^{-1}$  of TC under visible light radiation reached the photodegradation rate of 77%. Also, MIP showed the TC-selective recognition and promoted the photodegradation of TC in the ternary solutions containing TC, oxytetracycline (Oxy), and ciprofloxacin (CIP). The coefficients of selectivity of degradation from TC, Oxy, and CIP were 1.67 and 1.25, respectively. The photodegradation mechanism of TC analyzed by mass spectrum (MS) indicated the TC decomposition step by step, resulting in  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and other gases.

A large number of antibiotics and their residues lead to the environmental emergence as a threat to indigenous microbial populations. The tetracycline (TC) ranks second in the global production and use. In spite of its consumption, environmental TC residues are very low ( $\mu\text{gL}^{-1}$  or nanogram  $\text{L}^{-1}$ ), but they are resilient, and the TC residues may cause a series of ecological environmental and human health effects, such as promoting the resistant bacteria. The photocatalytic with solar energy is green technology and capable of decomposing the organic pollutant to a nontoxic compound.

The molecular imprinting is a versatile and straightforward method for the preparation of robust materials which can recognize the specific target in secondary and tertiary systems. Then, stability, the ease of development, and low cost make the molecularly imprinted particularly



attractive. Two or more antibiotics always coexist in the polluted aquatic environment. Thus, it is essential and meaningful to discuss the multicomponent antibiotics solution.

Published works related a variety of antibiotics in polluted soil and water environment. Therefore, it is of great significance to explore the ecological risk of the combined exposure to various antibiotics. The mixture of different types of antibiotics may lead to varying joint effects on the bacteria's, synergistic, additive, and some antagonistic effects.

Some published works indicate that antibiotics mixtures present synergetic effects and others antagonistic effects. The presence of sulfonamides (SA), as potentiator effects (SAP), and tetracycline's (TC) was investigated for binary and tertiary mixture toxicity. The mixtures of SA-SAP and SA-SAP-TC presented a synergetic impact on bacteria tests, while SA-TC and SAP-TC showed antagonistic effects. The TC presence in ternary mixtures altered the toxic ratio of SA and SAP, which lead to the various joint effects of the ternary mixtures on different bacteria populations.

## 5. The biocarbon: adsorbent uses

Since the beginning, the powder biocarbon in Brazil was considered a worthless material, always related to airborne pollution, infant and slavery condition work, and work-related disease. Nowadays, a group of researchers is trying to restore the biocarbon industrial use as an essential additive for agroindustry on soil amendment with possibility of enhancing the organic matter and water content retention.

The biocarbon (biochar) has been used to increase the amount of organic matter in the agricultural soil. There are many benefits in this application, resulting in improved soil fertility, nutrient content, water retention, better physical structure, and improved microbial activity. Intense agricultural operation tends to reduce the amount of organic matter present in the soil.

The application of biocarbon can be decisive in the semi-arid region of the northeast region with low rainwater retention, and such water source is scarce and used in a short period of the year. Soon, the agriculturists of these areas will be able to produce the own bio-carbon utilizing the agriculture biomass.

The biocarbon organic matter composition allows its use as a slow-release fertilizer such as adsorbent properties promoting the addition, retaining and the release of nutrients. The addition of some plastic agents like stack gel and bentonite clay helps the nutrient releasing rate control during the pellets formation. The biocarbon is a renewable organic matter source and provides phosphate and nitrate from wastewater adsorption treatment with nutrient retention for further agriculture use as slow-release fertilizer.

Biocarbon produced in a high-temperature pyrolysis application on heavy metals retention such as cadmium and zinc is studied. In some cases, it has been used in the recovery of soils with different levels of cadmium, zinc, and leads contaminated by the mining industry, reducing the concentration of toxic metals in plants such as beans.



Biocarbon as an alternative adsorption matrix for water treatment and emerging pollutants removal has been confirmed. The biocarbon usually shows better environmental results in comparison with activated carbon, and also in many cases, it provides better potential energy supplied for lignocellulosic materials.

The biochar has various environmental applications like pollutant removal, carbon sequestration, and soil amendment. It has unique properties which makes it an efficient, cost-effective, and environmentally friendly material for contaminant removal. The different physical–chemical properties of the surface are microporosity and pH that can maximize its efficiency to various environmental applications. The research updates related to the pollutants interaction with surface functional groups of biochar and the effect of the parameters variability in biochar attribute to specific pollutants removal, involved mechanisms, and efficiency for these removals.

Emerging pollutants (EPs) include agrochemicals, antibiotics, polycyclic aromatic hydrocarbons (PAHS), polychlorinated biphenyls (PCBs), volatile organic compound (VOC), aromatic dyes, toxic metals, ammonia, nitrate, phosphate, sulfite from aqueous, gaseous, and solid phases. There is also the possibility of the biochar-tailoring properties to improve their removal efficiency for organic–inorganic contaminants [20]. The soil application not only remediates but improves soil properties as water-holding capacity, O<sub>2</sub> content, and moisture level.

The removal of aromatic dyes, for example, rhodamine, methyl violet, and methyl blue by anionic biochar, is mainly involved in electrostatic attraction/repulsion interactions [17, 18, 25]. In these sorption mechanisms, highly polar biochar pyrolyzed at  $\leq 400^{\circ}\text{C}$  contained aromatic  $\pi$ -configuration and electron donor and acceptor functional groups [20]. These  $\pi$  electron-rich biochar functional groups ( $-Ve$ ) have electron donor-acceptor interactions with  $\pi$  electron-deficient ( $+Ve$ ) organic dyes. Hence, these interactions have resulted in an electrostatic repulsion and promoted pollutant adsorption via H-bonding between biochar and apolar dyes [26].

Crop residues as peanut, canola, soybean straw, rice hull, and so on derived biochar at a temperature of  $\leq 400^{\circ}\text{C}$  contained more O- and H-bearing functional groups. Thus, such a material exhibited a higher sorption capacity for apolar methyl violet and methylene blue due to pH change through biochar amendment [17, 24]. At higher pH, the net negative charge on biochar surface (due to dissociation of phenolic OH groups) increased the electrostatic interactions with methyl violet, whereas at lower pH, the  $\pi$ - $\pi$  electron donor-acceptor interactions increased, thus improving the H-bonding for methylene blue sorption.

At zero point charge (ZPC), biochar does not have any surface charge, and it develops surface charge dependent on pH. The pH below the biochar ZPC (8.17, 8.52 and 8.79) comprised positive charge and sorbs less methylene blue. Whereas the pH higher of the biochars ZPC comprise negative surface charge increasing the methylene blue adsorption due high electrostatic attractions.

Likewise, the sorption of polar antibiotics sulfamethazine (SMZ) by hardwood/softwood-derived biochars (produced at  $300\text{--}700^{\circ}\text{C}$ ) has pH-dependent interactions. At higher pH, H bonding occurs between anionic SMZ and COOH or OH group biochar. At lower and neutral pH, the  $\pi$ - $\pi$  electron donor-acceptor interactions and cation exchange are dominant mechanisms

between biochar and SMZ [23, 26]. These studies confirmed that pH is the most crucial factor for biochar interactions with polar organic pollutants.

The integrated process of photodecomposition followed by adsorption study includes the adsorption isotherms, performing the calculations of Langmuir, Freundlich, and Redlich-Peterson (R-P) isotherms, Eqs. (7)–(9), respectively. The Langmuir isotherm adsorption assumes an ideal solid surface composed by a series of distinct sites capable of binding the adsorbate in a molecular coverage; the chemical reaction between the adsorbate molecule and the surface is a pseudo-second-order reaction. The Freundlich isotherm is empirical but widely used, and the value of  $n$  is a measure of the adsorption intensity higher than 1, where the adsorption processes are more favorable. The Redlich-Peterson (R-P) is more accurate than the Langmuir and Freundlich due the “ $g$ ” value equal to 1. Usually, the R-P is by Langmuir and Freundlich isotherm equations; such observed behaviors were also studied. The error calculation will help to point out better isotherm adjustment

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \quad (7)$$

$$\log q_e = \log K_f + 1/n \log C_e \quad (8)$$

$$\ln (C_e/q_e) = g \ln C_e - \ln K_r \quad (9)$$

where  $C_e$  = equilibrium concentration ( $\text{mgL}^{-1}$ ),  $q_e$  = the amount adsorbed at equilibrium ( $\text{mg.g}^{-1}$ ),  $Q_0$  and  $b$  are Langmuir constants,  $Q_0$  indicates the adsorption capacity of the material, and  $b$  indicates the energy of adsorption.  $K_f$  and  $n$  are Freundlich constants.  $K_f$  indicates the adsorption capacity of the material and  $n$  indicates the efficiency of adsorption.  $K_r$  and  $g$  are Redlich-Peterson constants;  $K_r$  indicates the adsorption capacity and “ $g$ ” is the exponent between 0 and 1.

The RL values were in the interval from 0 to 1, with favorable adsorption accordingly with Langmuir isotherm. The Freundlich isotherm constant  $n$  was also in the range of  $2 < n < 10$ ; the indication of the agreement with Freundlich model with equal adsorption heating and Redlich-Peterson parameters were also promising.

## 6. Conclusion

The emerging pollutants are considered potentially toxic chemicals present in low concentrations and many environmental compartments. They include pesticides, biocides, pharmaceuticals, industrial chemicals, and personal care products. The common entrance of these compounds in surface water resources is via untreated sewage discharge, the effluents of wastewater treatment plants (WWTPs), and from agricultural, urban, and street runoff. The organic pollutant water inputs usually occur continuously in low dosages or as peaks triggered by emission or runoff events. Such a behavior is particularly harmful to antibiotics environmental contamination, providing the optimized conditions for microorganism adaptation

and increase in resistance. The concept of chemical activity helps to understand the EPs environmental fate, distribution, quantification, and prediction of the ecological partitioning theory of the chemicals in aquatic systems as water column, sediment (mostly organic matter), and biota (lipids and proteins) address single compound or mixtures reaching the equilibrium. The chemical activity relies on partition coefficients which are only available as experimental values.  $\text{TiO}_2$  has emerged as a promising photocatalyst for environmental cleanup applications; they have efficiently decomposed and removed a variety of pollutants, promoting the generation of OH radicals using oxidation reactions with in situ active oxygen generated upon light irradiation. In water purification, photodegradation of contaminants in real water samples has become an important topic of research in recent years. The results of the kinetics studies of photodecomposition and carbon sorption provide valuable insights about the kinetics models: pseudo-first-order (Eq. (1)), pseudo-second-order (Eq. (2)), and intraparticle with the determination of photodecomposition and adsorption rates. The ESI-MS analytical technique allows the measurement of the EPs methylene blue photodecomposition. Before the photodecomposition reaction, the methylene blue compound was only  $m/z$  284, and after 1 day of photodecomposition, there are several peaks.

The UV spectra of amoxicillin (AMX) and the amoxicillin decomposition products (ADPs) as ADP1,2, ADP4,5, and ADP8,9 consisted of two peaks at  $\lambda = 230$  and  $275$  nm, similar with AMX. This effect is due to the para-substituted phenolic group, which do not change in the AMX and ADPs skeleton and is the primary contributor to the observed UV spectra. The development of analytical technique allows the identification and quantification of the ampicillin and ampicillin degradation by-products as 2-hydroxy-3-phenylpyrazine (HPP) in the environment. The results indicate their presence in 42–79% of the monitored rivers and household ponds. In these locations, the HPP concentrations were in the range of  $1.3\text{--}413.3\text{ ngL}^{-1}$ . The amoxicillin and many antibiotics can act as a complex ligand with several possible sites for metal ions like Cu (II), Zn (II), and Cd (II) for coordination on penicillin. The kinetics and thermodynamics calculations indicate neighboring group effects of the probable complexation sites, of metals and the C=O of the antibiotic  $\beta$ -lactamic group and the NH amido penicillin group. Published works related to a variety of antibiotics in polluted soil and water environment. Therefore, it is of great significance to explore the ecological risk of the combined exposure to various antibiotics. The mixture of different types of antibiotics may lead to varying joint effects on the bacteria, synergistic, additive, and some antagonistic effects. The biocarbon acts as an alternative adsorption matrix for water treatment and emerging pollutants removal, usually showing better environmental results in comparison with activated carbon, and also in many cases, it provides better potential energy supplied for lignocellulosic materials.

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