

Combined Microwave-Peanut Hull Based Activated Carbon Process in the Removal of Oxytetracycline (OXT) from Aqueous Solution

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ABSTRACT: Carbon materials are gaining importance in catalytic processes. In this respect, the authors studied the most important characteristics of these materials when employed as catalysts for the removal of pollutants from wastewater. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FT-IR) were used to characterize Charcoal Activated (CA) derived from the chemical activation of peanut hulls. The key physical characteristics of the solids used in heterogeneous catalysis are the pore volume, the pore distribution, iodine number, oxygen surface groups, and the specific surface area. The combined microwave radiation-CA catalytic activity was assessed through the degradation of Oxytetracycline (OXT) under different irradiation times, initial concentrations, and acidity of the OXT solution. Furthermore, the effect of additional amounts of derived CA on the degradation was assessed. A higher removal rate of OXT contaminant by a combined MW-CA process was a synergic effect and was achieved at a low concentration of OXT and pH 3 (which is the pH range of OXT solution). Furthermore, an additional amount of CA increased removal efficiency. These favorable properties make carbon a viable alternative for use as a catalyst with no residual intermediates or secondary pollution.

KEYWORDS: Catalysis; Activated carbon; Characterization; Synergetic effect; Oxytetracycline.

INTRODUCTION

The antibiotics present in the environment and particularly in surface water constitute a major environmental [1].

Microwave catalytic technology can be highly efficient for the degradation of macromolecular organic pollutants [2].

Activated carbons or Charcoal-Activated (CA) are

known to be very effective adsorbents due to their well-developed porosity, large surface area, variable characteristics of surface chemistry, and a high degree of surface reactivity [3 - 9]. These characteristics, which make CA very versatile materials, have encouraged research into their

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1021-9986/2022/6/1896-1906 11/\$/6.01

Table 1: Physical properties of Oxytetracycline.

| Empirical formula | Molecular weight | Melting point | Physical status | pKa |
|---|------------------|---------------|-----------------------|------------------|
| C ₂₂ H ₂₄ N ₂ O ₉ | 460.4 g | 182°C | Solid (yellow powder) | 3.3, 7.3 and 9.1 |

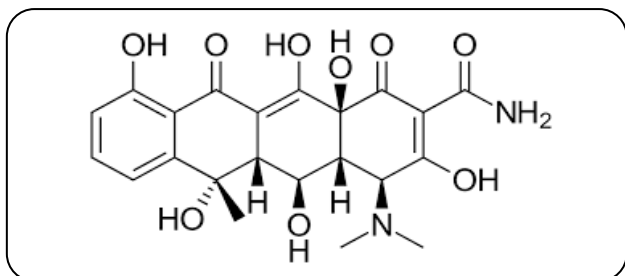


Fig. 1: Chemical formula of Oxytetracycline.

use as adsorbents as well as catalysts and catalyst supports for different purposes such as pollutants removal from gaseous or liquid phases and for the purification or recovery of chemicals [10].

A key challenge in the area of activated carbon production is to develop specific materials with desired properties such as surface and porosity, from low-cost and low-temperature precursors [11].

The novel approach suggested here is based on the development of low-cost adsorbents, in particular with waste materials. Moreover, to assess the catalytic activity of the activated carbon, microwave irradiation was employed to remove Oxytetracycline (OXT) from the liquid phase.

Few studies have investigated the degradation of such antibiotics under microwave irradiation [12 - 15], and still, fewer have been devoted to the possibility of using activated carbons prepared from agricultural wastes as a catalyst in the microwave process for the removal of these molecules. We compared the results with those obtained by simple adsorption on CA, which were the subject of previous work from our team [16].

Results show that this technology offers numerous advantages such as a high degradation ratio, short irradiation time, simple equipment, no residual intermediates, and no secondary pollution.

EXPERIMENTAL SECTION

Chemicals

Sodium hydroxide (NaOH), hydrochloric acid (HCl), iodine (I₂), and phosphoric acid (H₃PO₄) were purchased from Merck (Merck Darmstadt, Germany), and

Oxytetracycline (pollutant) from Sigma (Sigma-Aldrich, Taufkirchen, Germany). Its structure is given in Fig. 1 and its main physicochemical properties are summarized in table 1. All chemicals used are the highest purity and were used without further purification.

The charcoal activated was washed adequately with deionized water and then dried at 105 °C for 6.0 h to constant weight. The activated carbonaceous material obtained from peanut hulls (Fig. 2) was called CA.

Characterization of CA

Activated carbon CA was characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform InfraRed (FT-IR) spectroscopy. The main physical characteristics of the solids employed in heterogeneous catalysis are the pore volume, the pore distribution, iodine number, oxygen surface groups, and the specific surface area.

The 77K nitrogen adsorption-desorption isotherm was used to characterize the internal texture of activated carbon and the iodine number was determined using the experimental protocol proposed by ASTM [17]. The determination of the point of zero charges (pH_{PZC}) was conducted to investigate how the surface charge of CA adsorbent depends on pH. pH_{PZC} of the activated carbons was determined using the procedure described in [18].

XDR patterns were carried out by using X-Ray Rigaku DMAX diffractometer using Cu -K α radiation as a source of radiation which operates at a wavelength of 1.5518 Å.

Emission Scanning Electron Microscopy (FESEM) and Dispersive X-ray spectrum analysis (EDX) were carried out on OCTAN PRO microscope from EDAX AMETEX with a voltage of 20 KV supported by EDAX-Genesis software. Optical properties were carried out on a UV-JASCO V-650 spectrometer. The IR spectra were obtained by analyzing the prepared compound on FT-IR Nicolet Avatar 330 model, whereas the scanning range was 4000 - 400 cm⁻¹.

Procedure

The catalytic activity of CA was investigated by degradation experiments using OXT under microwave



Fig. 2: Synthesis process of CA.

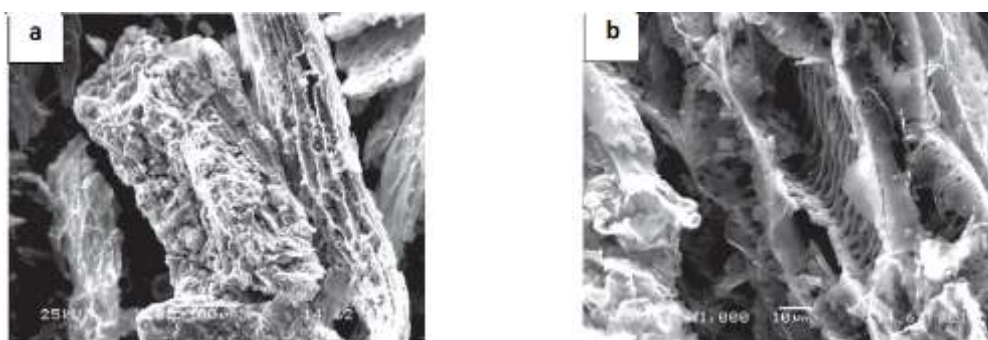


Fig. 3: SEM image of raw CA at different magnifications (a: 100 μm and b: 10 μm).

irradiation. In each experiment, 0.025 g of catalyst was added under stirring to 25 mL of 50 ppm OXT solution. At specified intervals of reaction; the solution was quickly sampled and cooled down to room temperature. In addition, UV-vis spectra of OXT solutions at different irradiation times were also determined and the corresponding degradation ratios were calculated. Moreover, to verify the reliability of the calculated degradation ratios, the Chemical Oxygen Demand (COD) values of the treated solutions were determined.

Besides, in order to confirm that all OXT on the surface of the activated carbon (CA) were degraded under microwave irradiation, FT-IR spectra of CA were determined in the wave number range 400 - 4000 cm^{-1} . For comparison, the FT-IR spectrum of the original CA was also given. Moreover, the influences of the initial concentrations (20 - 250 mg/L) and addition dose (0 - 3.5 g/L) of CA and initial pH (1.0 - 12.0) of OXT solutions on degradation were reviewed in this work.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)

Grain morphologies of CA powder can be observed from SEM image represented in Fig. 3. One can clearly see the macropores, the micro-, and mesopores at the surface of the material. It can also be seen that the surface morphologies of the elaborated activated carbon CA is abundant, and the availability of pores and the internal surface are clearly displayed in the image.

Energy Dispersive X-Ray Spectroscopy (EDS) spectrum result

The working principle of the EDS technique consists of using X-rays emitted from the sample during bombardment by an electron beam to determine the elemental composition of the analyzed volume on a micro- or nano-scale [19].

EDS analysis (Fig. 4 and Table 2) revealed a weight percentage of 77.68 carbon and 15.42 of oxygen on the NP

Table 2: EDS elemental analysis of CA.

| Element | C | O | Na | Mg | Si | P | S | Cl | K | Ca |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Wt% | 77.68 | 15.42 | 00.18 | 01.30 | 00.14 | 00.49 | 01.36 | 00.45 | 00.44 | 02.54 |
| At% | 84.62 | 12.61 | 00.10 | 00.70 | 00.06 | 00.21 | 00.55 | 00.17 | 00.15 | 00.83 |

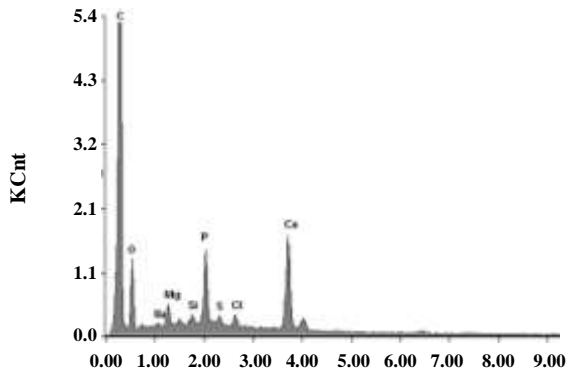


Fig. 4: EDS spectrum of CA.

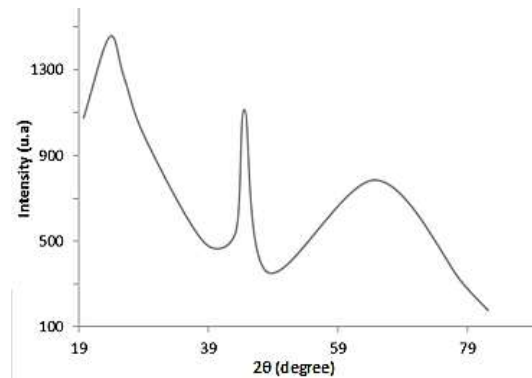


Fig. 5: XRD pattern of CA.

the surface of CA. It has an atomic percentage of 84.62 carbon and 12.61 oxygen.

The spectrum indicates the presence of other basic elements called catalyst dopants, which are responsible for the catalyst acidity and can adjust the porous texture. These include phosphate, calcium, magnesium, and silicon [20, 21]. This result is confirmed by the pH_{PZC} value (Table 2) which indicates the basic character of CA [22, 23].

XRD Analysis

Fig. 5 shows the XRD pattern of the prepared CA. This situation suggests, once again, that some residues contaminated the isolated product. Fig. 5 generally shows an amorphous structure of the material studied and low crystallinity of the sample in the range from 10 to 70°. The peaks of diffraction at 23.789° and 44.617° are attributed to carbon black graphite-like material [24 - 29]. The broad peak located around 64.824° is affected at mixed phases of cellulose-impregnated and alkali earth metal salts ($M = \text{Ca}, \text{Mg}$ and Si) [30 - 32]. These alkali earth metals are identified by EDS investigation (Fig. 4).

Porosity characterization

The prepared activated carbon CA was subject to the measurement of iodine number, pH_{PZC} , and BET surface area. The iodine adsorption capacity is represented as the iodine number, which indicates milligrams of iodine

adsorbed by a gram of activated carbon, to test the acting activated carbon. The BET surface area and the average pore size distribution are estimated using the surface area analyzer. Estimation of the average pore radius r_p is performed by applying the equation below [19]:

$$r_p = 2V/S_{\text{BET}} \quad (1)$$

Where V (cm^3/g) is the total pore volume and S_{BET} is the BET surface area. Table 3 summarizes the properties of the prepared activated carbon.

The average pore radius r_p was calculated using Equation (1) and the r_p size is ≈ 1.26 nm. Analysis of the pore structure indicates that the material is dominated by microspores i.e., those pores are less than 2 nm.

The pH_{PZC} is an important indicator for any activated carbon as it shows the acidity/basicity of the adsorbent and the net surface charge of the carbon in the solution. At $\text{pH} < \text{pH}_{\text{PZC}}$, the carbon surface has a net positive charge, while at $\text{pH} > \text{pH}_{\text{PZC}}$, the surface has a net negative charge [33]. The pH_{PZC} value for CA is 8.2, which indicates the basic nature of the carbon in the solution.

Process comparison

The influence of the individual contributions of the microwave oxidation (MW) and CA adsorption processes on the hybrid process (MW-CA) was analyzed. Fig. 6

Table 3: Porosity characterization of CA.

| | CA |
|--|--------|
| SBET (m ² /g) | 481.45 |
| Micropore volume (cm ³ /g) | 0.19 |
| Total pore volume (cm ³ /g) | 0.304 |
| r _p (nm) | 1.263 |
| Iodine number (mg/g) | 2.286 |
| pH _{pzc} | 8.2 |

Table 4: Process comparison.

| Process | MW | Adsorption onto CA | CA + MW |
|-------------------------|-------|--------------------|---------|
| R% | 8.97 | 25.40 | 63.39 |
| r ₀ (mg/L.s) | 0.014 | 0.069 | 0.192 |

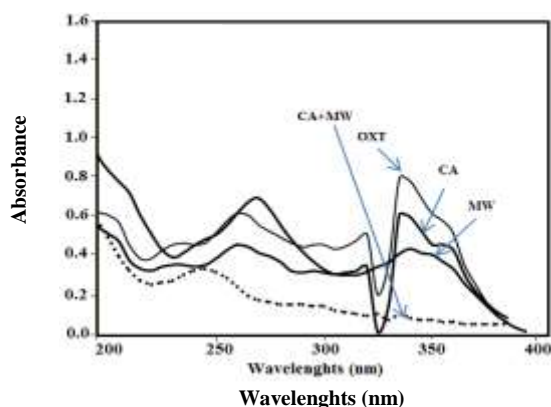


Fig. 6: UV spectrum of OXT solutions (according to the absorption peak at 354 nm). Experimental conditions: OXT concentration of 50 mg/L, CA dose of 2 g/L, and total volume of 25 mL. MW (120 s), CA, and MW-CA (600 s).

shows that the best results to mineralize the antibiotics are achieved by the MW-CA hybrid process.

This can be explained by the synergistic effect of the processes involved. It can also be seen that the degradation ratio and the initial reaction rate (Table 4) decreased slightly under one-fold activated carbon adsorption, which meant that only a few OXT molecules were degraded, and the corresponding degradation ratio is about 25.40%.

Activated carbon (CA), as an excellent MW-absorbing material [16], could absorb and convert MW energy into thermal energy, microwave irradiation can accelerate the elimination of organic pollutants is the formation of "hot spots" on the surface of CA [34, 35].

Evaluation of the synergistic effect

In order to evaluate if there exists a beneficial interaction between the adsorption onto CA catalyst and MW irradiations, *Salatiel Wohlmuth da Silva et al.* proposed a formula (Eq. (2)) that measures the synergistic effect (or on the contrary the antagonistic effect) of the treatment by the hybrid process [36]:

$$s = \frac{k_{MW+AC(PH800)} - (k_{MW} + k_{CAPHAC(PH800)})}{k_{MW+AC(PH800)}} \quad (2)$$

Where K is the first order rate constant with, in the index, the treatment applied. Here, the effect is synergistic if s is positive, and antagonistic if it is negative.

The results of Table 5 clearly show the existence of a synergistic effect between the adsorption and the MW irradiation processes.

Spectral analysis of CA

The FT-IR spectrum of the activated carbon both after and before MW-CA experiments is compared to the FT-IR spectrum of the saturated activated carbon after adsorption treatment as shown in Fig. 7.

The comparison of this spectrum with that of the raw CA clearly shows that the two activated carbons are similar since we note the same peaks that we assign to C-H, N-H, C-C functional group bonds.

The comparison with that of the saturated CA spectrum shows an increase in the intensity of the entire peak after adsorption.

This increase demonstrates (i) a change in the characteristic

Table 5: Evaluation of the synergistic effect.

| Process | CA | MW | CA + MW |
|------------------------|--------|-------|---------|
| K (min ⁻¹) | 0.038 | 0.086 | 0.145 |
| S | 0.1448 | | |

Table 6: COD analysis results.

| Process | COD (mg/L) | Abatement rate (%) |
|----------------------|------------|--------------------|
| Initial OXT solution | 67.2 | / |
| MW | 76.8 | / |
| MW + CA | 28.8 | 57.14 |

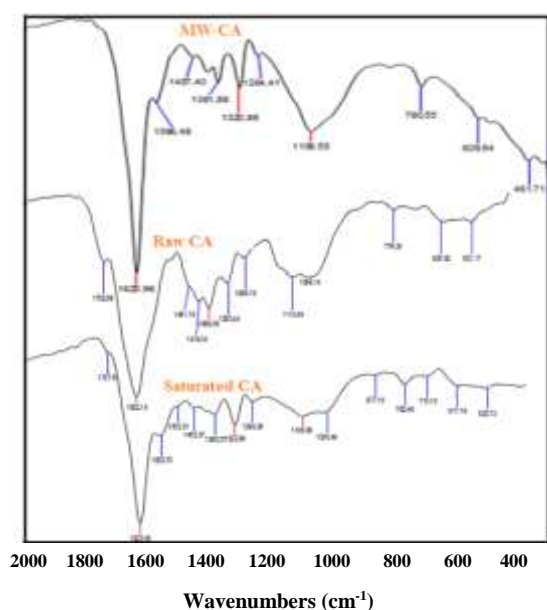


Fig. 7: FTIR spectrum of the raw, saturated CA and MW-CA residue. Experimental conditions: OXT concentration of 50 mg/L, CA dose of 2 g/L, and total volume of 25 mL. microwave (120 s); b: CA (600 s) and CA+MW (600 s).

of the activated carbon surface and (ii) chemical interaction between the OXT molecule and CA surface.

COD analysis

COD is used as a general indicator of water quality and is an integral part of all water quality standards [37]. To investigate the mineralization of OXT antibiotic molecules under MW irradiations in the presence of CA as a catalyst, COD is measured before and after the MW+CA experiment. The basic principle of the assay involves measuring the amount of COD removed after each experiment's test (in percent of initial COD).

The results of the COD measurements (Table 6) clearly illustrate the effectiveness of the MW+CA treatment. The COD measurements of the MW process show a value greater than that of the initial COD. This can be accounted for by the appearance of toxic by-products in solution arising from OXT degradation under microwave irradiations.

Influence of microwave irradiation time on degradation of OXT

As shown in Fig. 8, the influence of microwave irradiation time on the degradation of OXT from 0 s to 1200 s at 120 s intervals is reviewed in detail. This concentration of OXT in solution is found to decrease gradually with increasing irradiation time.

Influence of initial concentration of OXT on its degradation

The initial concentration of an organic pollutant is a key parameter in the wastewater treatment process. The initial concentrations of OXT solutions in this work varied from 20 to 250 mg/L. The results in Fig. 9 clearly indicate that the removal rate of OXT in 20 mg/L solutions is above 86% under microwave irradiation with CA. On the other hand, the corresponding degradation ratio was only 27% for the OXT in 250 mg/L solutions under the same conditions. As well known, there are limits to the activity of any catalyst. Indeed, the active sites on the surface of the activated carbon are finite and as a result, the amount of degraded OXT under microwave irradiation is limited within a certain irradiation time.

In addition, in the concentrated solutions, too many OXT molecules may disrupt the transmission and absorption of microwave energy, which can also lead to a decline in the catalytic activity of CA.

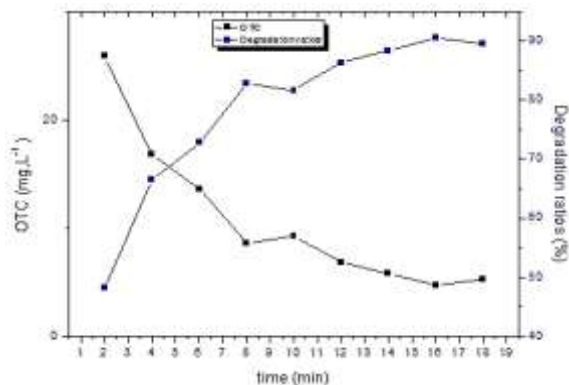


Fig. 8: Influence of microwave irradiation time on degradation of OXT. Experimental conditions: MW+CA, OXT concentration of 50 mg/L, AC dose of 2.0 g/L, solution acidity of pH=3.98, and total volume of 200 mL.

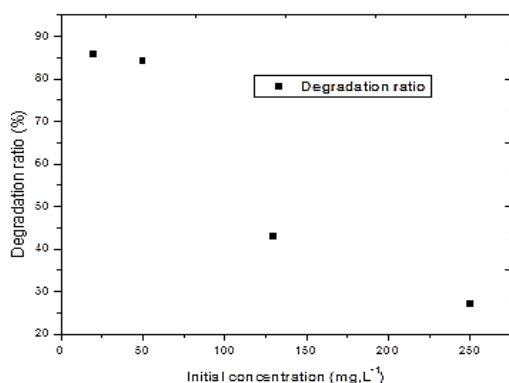


Fig. 9: Influence of initial concentration on degradation ratio of OXT. Experimental conditions: CA dose of 2 g/L, solution acidity of pH=3.94, irradiation time of 120 s, and total volume of 50 mL.

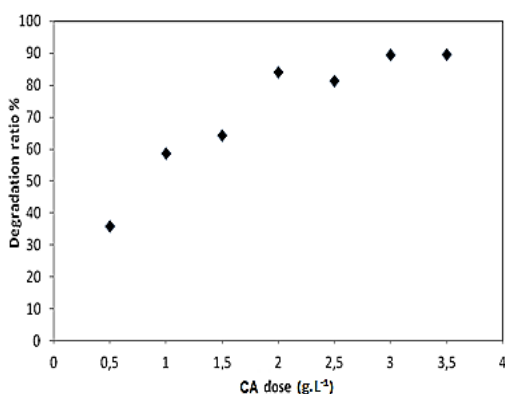


Fig. 10: Influence of additional amount of CA on degradation ratio of OXT. Experimental conditions: OXT concentration of 50 mg/L, solution acidity of pH=3.98, irradiation time of 120 s, and total volume of 25 mL.

Influence of additional amount of CA on the degradation of OXT

Considering the degradation rate and treatment cost, we studied the influence of the dose of the catalyst on the performance of the suggested process. In the present work, we conducted a series of experiments using CA from 0.0 to 3.5 g/L. As expected, Fig. 10 shows that the increase in CA amount resulted in accelerated degradation of OXT.

As one can clearly see, the degradation ratio rose rapidly at a low dose (from 0.0 to 1.5 g/L) but exhibited a relatively slow increase at a high dose (from 2 to 3.5 g/L).

Influence of solution acidity on the degradation of OXT

The pH value is considered one of the most important parameters that affect the way OXT behaves and evolve in an environment [38, 39]. Oxytetracycline, the subject of this study, is a large molecule with several polar/ionic groups and three environmentally relevant pKa values (Fig. 11) [40, 41].

In the range pH 4 to 8, OXT predominantly presents as a zwitterion, with a positive charge on the tertiary amine functionality and a negative charge on the deprotonated hydroxyl group.

The influence of the pH value as an essential parameter in the degradation reaction was therefore investigated (Fig. 12). Here, the pH value changed in the range 1.0 - 11.0. The pH was adjusted to the pre-determined value using NaOH or HCl solutions prior to the addition of the adsorbent.

The initial pH of the solution does not play an important role only on the zwitterionic OXT, but also in the surface charge properties of the sorbent.

From Fig. 12, it can be seen that the optimized pH for OXT removal by CA under MW irradiations is pH 3, 7, and 9, respectively. The highest degradation ratios of OXT are obtained when the pH is close to pKa.

The (microwave –adsorption) mechanism of OXT

It seems that the (microwave-adsorption) mechanism of OXT is the following: at the beginning, the OXT molecules in an aqueous solution are firstly adsorbed on the surface of CA catalyst (Fig. 13). As CA is an excellent microwave absorbent, hot spots can take place on its surface. As a microwave has a very strong penetrating ability in liquid media, microwave irradiation can make the polar molecules rotate fast, which brings obvious thermal effects [35, 42].

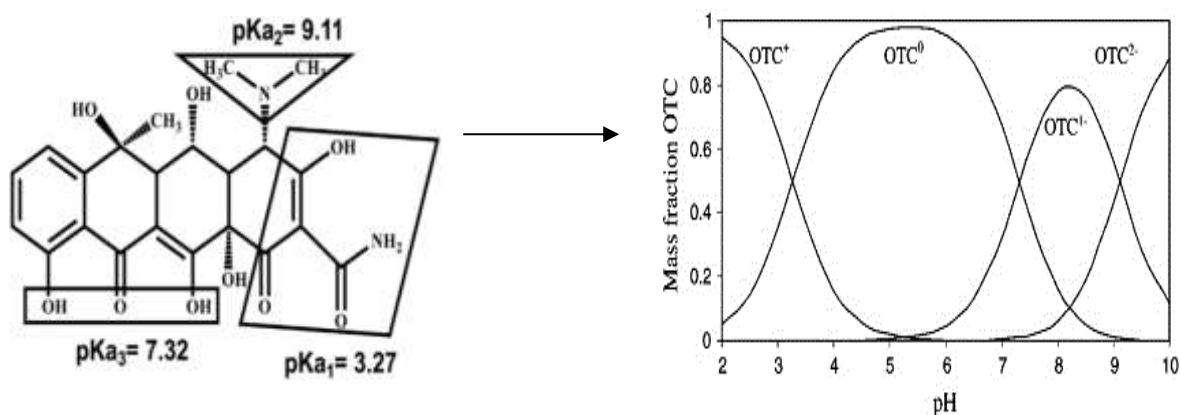


Fig. 11: Speciation diagram of Oxytetracycline.

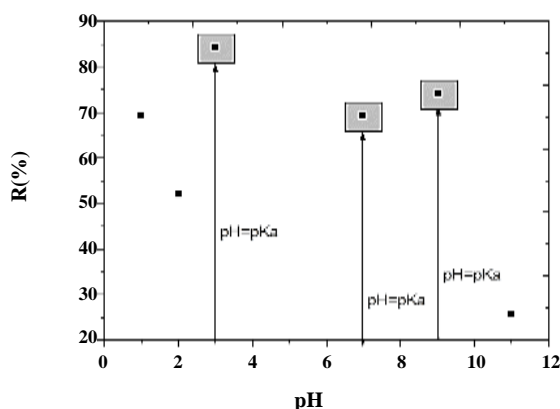


Fig. 12: Influence of solution acidity on the degradation ratio of OXT. Experimental conditions: OXT concentration of 50 mg/L, CA dose of 2.0 g/L, irradiation time of 120 s, and total volume of 50 mL.

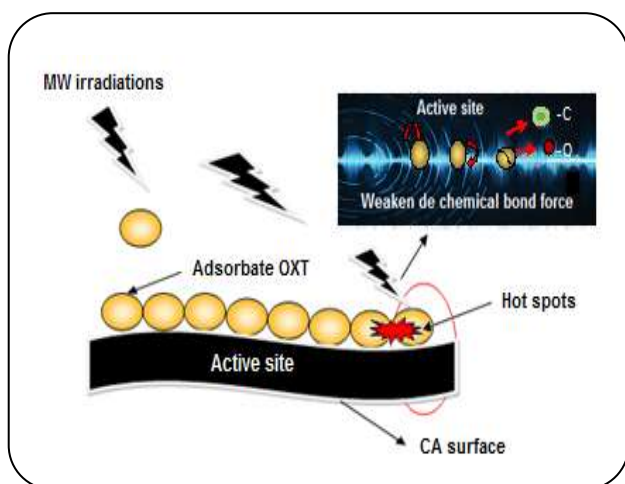


Fig. 13: Microwave-adsorption mechanism of OXT.

At the same time, the combined process can equally change the thermodynamics function, reduce the activation energy of the reaction system, and weaken the chemical bond intensities of OXT molecules. Although the adsorption phenomenon occurred, the OXT organic pollutant molecules adsorbed on the surface of CA would eventually be oxidized and degraded under microwave irradiation. Due to thermal effects, not only some simple chemical bonds such as C-N and C-C of the OXT organic pollutant can be destroyed, but also the benzene nuclei would be rapidly degraded.

CONCLUSIONS

The catalytic activity of the elaborated activated carbon CA was examined and this study has the merit of revealing the catalytic potential of CA to oxidize Oxytetracycline antibiotics under microwave irradiations.

A higher removal rate of OXT contaminant by combined MW-CA process was achieved at a low concentration of OXT and at pH = 3 (which is the pH range of the OXT solution). Furthermore, the additional amount of CA increased the removal efficiency of OXT antibiotics.

The adsorption capacity of CA is limited for any concentrated organic pollutants; therefore, many organic molecules cannot be completely removed through this process alone. Although the adsorption phenomenon occurred, those organic pollutant molecules adsorbed on the surface of CA would eventually be oxidized and degraded under microwave irradiation.

The nano-particles of CA have favorable properties for use as a catalyst with no residual intermediates and no secondary pollution.

Acknowledgments

The work was supported by « la Direction Générale de la Recherche Scientifique et Technologique (DGRSDT) » of Algiers-Algeria. The authors are gratefully acknowledged.

Received : May 22, 2021 ; Accepted : Aug. 2, 2021

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