Algerian Journal of Chemical Engineering 01 (2021) 16–23

Algerian Journal of Chemical Engineering

Journal homepage: http://www.ajce.periodikos.com.br/

Original Article

Microwave assisted preparation of onion skin activated carbon: Application for removal of tetracycline

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ARTICLE INFO

Article history:
Received 10 January 2021
Revised 25 March 2021
Accepted 07 Avril 2021

Keywords:
Adsorption;
Activated carbon;
Tetracycline;
Microwave.

ABSTRACT

The activated carbon prepared from onion skin by H_2SO_4 activation under microwave radiation was investigated. The effect of different condition in order to obtain the high removal efficiency of Tetracycline and carbon yield was studied. The optimum condition has been identified at the acid concentration of 1N, Microwave power of 720W, microwave radiation of 5min and impregnation heating time of 48 h. The obtained activated carbon under these conditions was characterized by scanning electron microscopy and by FTIR spectra. Microwave energy is predicted to be for fuel technology in various areas, while its progress represents an expanding field in the area of adsorption science.

1. Introduction

Antibiotics, such as tetracycline constitute a significant pollutant load both on the environment and on the aquatic environment. The large and irregular use of antibiotics in human and veterinary medicine leads to the arrival of a large amount of in the aquatic environment due to their incomplete metabolism. Additionally, the conventional water treatment systems cannot eliminate theses medicaments substances effectively [1].

Presence of TC and other antibiotics in natural environments can cause bacteria to acquire and transmit antibiotic, resistant genes which potentially threaten ecosystem functions and human health [2,3]. Therefore, to minimize the ecological risks of the TC, it is necessary to develop effective and low-cost treatment technologies for removal of this pollutant from aqueous medium. A simple method for removal of pollutants without continuous need of the chemicals is adsorption, especially; adsorption by activated carbon (AC).The disadvantage of this method is its relatively high cost. [5,6]. Consequently, many studies on the development of low cost activated carbons using wastes and agricultural compounds were developed [7-12]. Many natural materials available in large quantities may have great potential as low-cost adsorbents such as onion. 105 billion pounds of onions were produced each year, according to the estimate of the United Nations Food and Agriculture Organization. H_2SO_4, which is a powerful dehydrating agent, can react with organic compounds (*i.e.*, carbohydrates and other organic substances) removing water and degrading the organic precursor to elemental carbon H_2SO_4 can promote a partial degradation of the cellulose and hemicelluloses fraction, manly *via* a dehydration reaction, leaving a modified lignin residue. Thus, the use of H_2SO_4 for carbonization purpose may be advantageous as far as process cost (H_2SO_4 is a little expensive chemical) and chemical composition of AC is concerned. Also, it may use in the preparation of AC with different porous structures [13,14]. The pores in the carbon structure are further developed by chemical activation

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http://dx.doi.org/10.5281/zenodo.4670571

using H_2SO_4, and the carbon yields are generally high [15]. For preparation of activated carbons, the conventional heating method is usually adopted, in which the energy is produced by convective or conductive heating system. In the common practice, the removal process may take long processing time to reach its desired level of activation. Furthermore, there is a considerable risk of overheating or even thermal runaway of local sample, leading the complete combustion of the carbon [16,17]. However, it should be noted that the conventional thermal technique demands larger processing time and energy intensive, necessitating the need for alternative methods for the preparation of activated carbon. Recently, microwave irradiation has been widely investigated due to its capability of molecular level heating which led to homogeneous and quick thermal reaction [18,19]. The main advantage of the microwave heating is the reduction of the treatment time, which reduces the energy consumption, other advantages are as follows: interior heating, high heating rate, selective and controllability of the heating process, reduced equipment size, waste, and the consumption [5, 19-21].

Onions are gown all over the worlds. To our knowledge, there is not any work on the preparation of activated carbon using sulfuric acid from onion skin. The present work is aimed at evaluating the operational conditions for further improve the porosity development of the preparation of AC using onion skin by chemical activation with H_2SO_4. Then, the adsorption capacity of the AC prepared was examined. The influences of radiated power, radiation time and initial concentration of chemical agent on the yield of carbon and the percentage of TC were investigated systematically. Morphological structure and functional chemistry of the prepared adsorbent was performed.

2. Materials and Methods

2.1. Material

The onion skin used in this study was from the country, Algeria. The precursor was washed and was air dried, crushed and then sieved to obtain a particle size <1.6mm. Sulfuric acid was in analytical grad. Tetracycline hydrochloride<96% were obtained from Fluka-Sigma – Aldrich.

2.2. Methods

Activated carbon was prepared under different conditions. The effect of sulfuric acid concentration, impregnation heating time, microwave power and radiation time, on the removal of TC from aqueous solution and on the yield of carbon was studied.

The granular onion skin was added to sulfuric acid with different concentration for (0.5, 1, 1.5 and 2N). Samples were placed in the oven at 70 °C at different times (6-48h). The impregnated samples were heated in a microwave oven (STARLIGHT SL -MG model) with different powers (300-720W) and radiation time ranging from 1 to 15min). The obtained samples were washed for several times with distilled water to neutral pH, and dried in an oven at 110 °C for 6h. Finally, resultant obtained carbons were crushed and stored in a glass bottle. The obtained samples in different conditions were listed in table 1.

Table 1. Prepared samples in different conditions.

Activated carbon	**Power radiation (W)**	**Radiation time (min)**	**Sulfuric acid (N)**	**Heating impregna -tion time (h)**
CA_1		5		
CA_2	360	10		
CA_3		15		
CA_4		5		
CA_5	540	10	1	25
CA_6		15		
CA_7		5		
CA_8	720	10		
CA_9		15		
CA_{10}			0.5	
CA_{11}			1.5	25
CA_{12}	720	5	2	
CA_7				5
CA_{13}			1	25
CA_{14}				48

The different steps in the preparation of activated carbon were illustrated in the Fig.1.

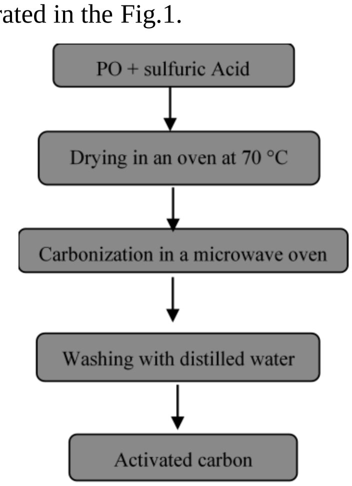


Fig.1. Different steps in the preparation of activated carbon.

The effect of the different parameters on the removal of TC efficiency (R_{TC}) and the carbon yield (R_{AC}) was studied. 50 ml of TC with certain concentration was agitated with 1g of adsorbent at 400 tr/min and 25 °C for 1h. The R% was calculated by:

$$R_{TC} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

$$R_{AC} = \frac{m}{m_0} \times 100 \quad (2)$$

where C_0, is the initial concentration (mg/L), and C the residual concentration after certain time, m_0, is the initial mass of onion skin before carbonization and m is the mass of onion skin after carbonization.

Antibiotic concentration was quantified by UV-visible spectroscopy (Shimadzu UV-1800) [22-24]. Tetracycline compound absorbances were measured at 360nm.

The surface morphologies of the resultant simples were imaged using LEOSTERO can scan electron microscope. Chemical characterization of functional groups was detected by Fourier Transform infrared spectrometer(Alpha-P Bruker) in the scanning ray of 4000-400 cm^{-1}.

3. Results and Discussion

3.1 Effect of microwave power on the percentage removal of TC and carbon yield

The effect of microwave power on the percentage removal of TC and carbon yield were evaluated under the experimental condition of microwave time radiation 5min and sulfuric acid concentration of 1N. Figure 2 showed that while increasing microwave radiation power from 360 to 720W, the percentage removal of TC was increased from 0 to 69.8%. Hejazifar*et al.* [5] report that at low microwave power, the pore structure is not adequately developed, while for strong microwave powers, the pore structure will be more developed[5].The possible reason for these observations is that the reaction between sulfuric acid and precursor is faster at the higher microwave power which facilitated the development of the pore structure. Foo *et al.* were attributed the higher removal at higher power microwave power to the combined effect of internal and volumetric heating winding the existing pores [25]. Meanwhile, the carbon yield decreased proportional to the microwave power level, possibly due to the fierce reaction at higher thermal radiation, which resulted in greater weight loss of the carbon simple.

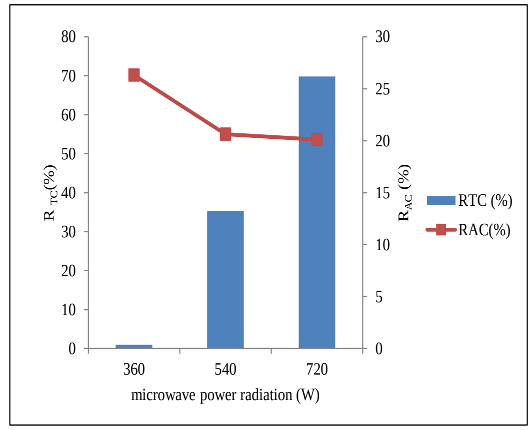
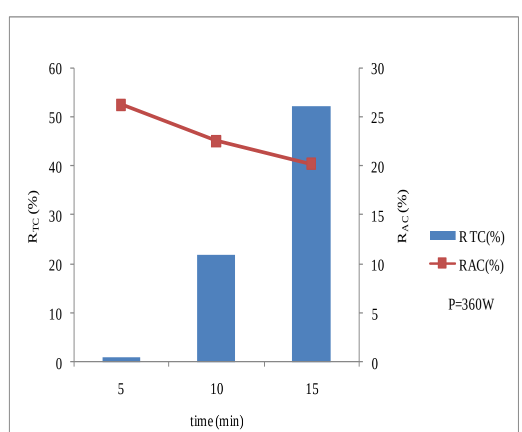
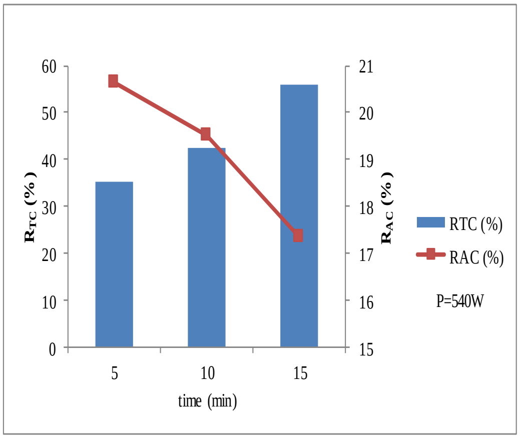


Fig. 2.Effect of microwave power (preparation conditions: sulfuric acid=1N, radiation time=5min, impregnation heating time 24h).

3.2 Effect of radiation time

Microwave radiation time is another decisive factor affecting the percentage removal and carbon yield. To study the effect of radiation time on the removal efficiency, a series of experiment were conducted. Other experimental conditions were set as sulfuric acid concentration 1N, impregnation time of 24h, and oven temperature of 70°C. As shown in Fig.3, the R_{TC}% increase with increasing the radiation time from 5 to 15min, when the microwave power was below the 540W. Meanwhile, the carbon yield was decreased with increasing the radiation time. The result implied that prolonging radiation time promoted an acceleration of energy, which in turn increased the reaction rates, thus developed the internal porosity of AC. When the power radiation passes to 720 W, an increase of removal efficiency was observed with only 5 min of radiation time. The phenomenon implied that the formation of new pores became less significant with activation proceeding and the micropores or mesopores were continuously widened into larger ones. So, the efficiency was also being reduced after long time exposure to the microwave radiation [26].





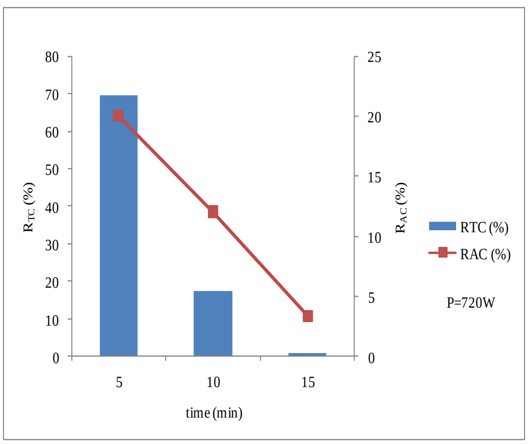


Fig.3.Effect of radiation time.

3.3 Effect of sulfuric acid concentration

Effect of sulfuric acid concentration on the carbon yield and removal efficiency of TC at the microwave power of 720W and irradiation time of 5min was depicted in Fig.4. It can be seen that increasing of sulfuric acid concentrations from 0.5 to 2N, showed an increase of removal efficiency, and then decreased. It can be also observed that augmenting a sulfuric acid concentration from 0.5 to 2N showed also a decrease of carbon yield. Foo and Hameed found that by increasing the concentration of H_2SO_4, the activation process would be enhanced, beyond the optimum value (in our case 1N), the excess of H_2SO_4 left on the precursor surface caused blocking of the pores leading to a dramatic decrease of accessible area [27]. Additionally, the pores would be widened lowering the removal efficiency and carbon yield. It is very import to note that a concentration of 1N is relatively weak compared to that used in other work [15,28,29].

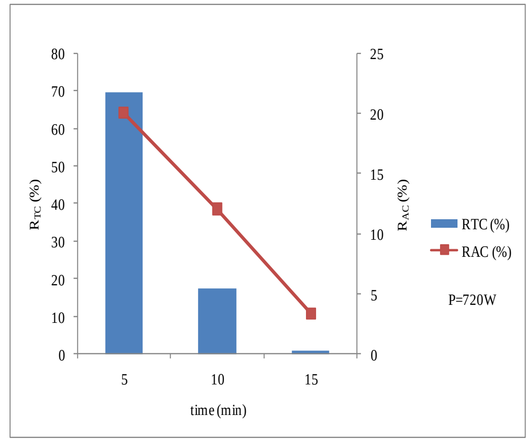


Fig.4. Effect of sulfuric acid concentration.

3.4 Effect of impregnation heating time

The effect of impregnation heating time (5-48h) on the R% was evaluated under the experimental condition of acid concentration (1N), Microwave power 720W, microwave radiation time 5min and oven temperature 70°C. Experiments for determination of R% were carried out with TC concentration by 20mg/L and contact time of 1h. Based on the result shown in Fig.5, the removal efficiency increased, proportional to the heating impregnation time, while the carbons yield decrease. These results can be explained as well as increasing the heating impregnation time can improve the activation process and some pores of activated carbon would be released, leading to the increase of the removal efficiency [30].

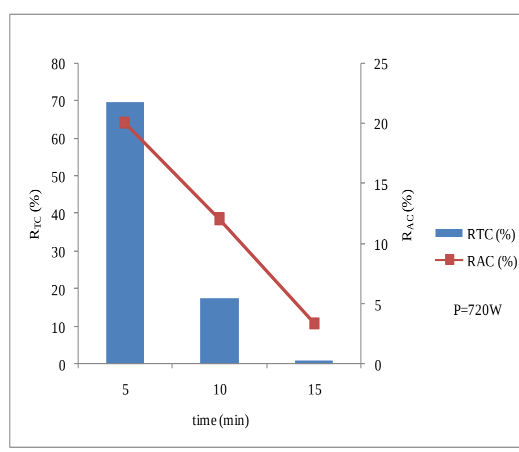


Fig.5. Effect of impregnation heating time.

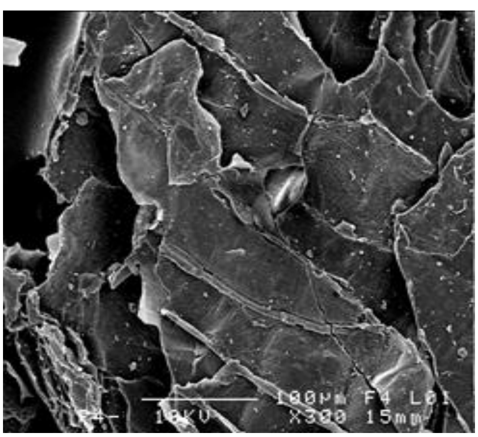
3.5 Characterization of prepared AC from onion skin

From the discussion mentioned above, radiation power, radiation time, acid concentration and heating impregnation time had affected the removal efficiency and carbon yield, therefore, AC used in characterization analysis were prepared under optimum conditions as follows:

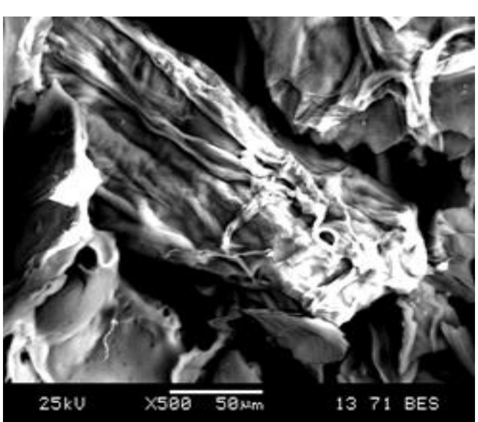
- Microwave power radiation time=5min;
- Microwave power 720W;
- Heating impregnation time 48h;
- Acid concentration=1N.

3.6 Surface morphology

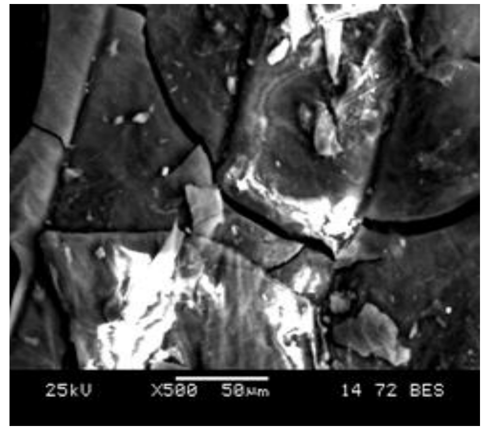
The scanning electron microscope (SEM) technique is widely used to study the surface morphology of the adsorbent materials. SEM image of the structure of the raw onion skin, the activated carbon prepared under optimum conditions, and then the activated carbon after adsorption of TC were shown in Fig.6. A significant difference of the surface topography between raw material and AC was observed. Some occasional crakes were observed on the activated carbon, resulting from the evaporation of the chemical reagent during carbonization, leaving the space being previously occupied by the reagents. After adsorption(Fig.6.c), we noted the presence of black tack on the surface, indicating the adsorption of TC.



(a)



(b)



(c)

Fig.6. Scanning electron microscope of (a) raw onion skin of AC_{14}; (b) before and (c) after adsorption.

3.7 FTIR analysis of AC_{14} after and before adsorption

The FTIR spectra of AC_{14} were scanned before and after TC adsorption (Fig. 7). In all recorder spectra 3600-330 cm^{-1}, the bands of stretching O-H vibrations are revealed which can be attributed to surface hydroxyl groups and physically adsorbed water. The band at 3144 cm^{-1} represents the presence of N-H groups.The observed at 2400 cm^{-1} can be assigned to C-H aliphatic vibration and methoxy aromatic methoxyls groups. The additional peak at 799 cm^{-1} and 666 cm^{-1} can be assigned to bending modes of aromatic compounds. The peak at 1700 cm^{-1} is attributed to the carbonyl (C-C=O) stretching from the carboxylic acid ketone or aldehyde groups. The band at 1126 and 1043 cm^{-1} indicate the presence of C-O of carboxylic groups. The FTIR spectrum of the activated carbon after adsorption TC shows:

- Offset in wave numbers of certain peaks;
- The shape of certain bands;
- Increase in the intensity of certain peaks.

This traduces the interaction between active coal sites and TC.

4. Conclusion

The present study reported a facile method to prepare activated carbons (AC) using a microwave as heating energy. The precursor used to prepare the activated carbon is the onion skin; it was chemically activated with H_2SO_4.The impregnation heating time and acid concentration on the removal efficiency and carbon yield were investigated. The optimal conditions of sulfuric acid concentration (1N), impregnation heating time (48h), microwave power (720W) and radiation time (5min) were obtained. Under these optimum conditions, the prepared

AC demonstrates an adsorption efficiency of tetracycline as high as 75%. Then, the AC sample prepared also under optimal conditions was characterized with FTIR analysis. The results of this analysis show the presence of oxygen-containing functional groups such as hydroxyl groups on the surface, and exhibit high adsorption capacity using TC as a model adsorbate because of the electrostatic interactions. The scanning electron microscopetechnique was used to study the surface morphology of the adsorbent materials. The AC prepared present a significant difference of the surface topography compared with the raw material. Microwave heating could shorter the processing time and reduce the consumption of H_2SO_4.

Conflict of Interest

The authors declare that they have no conflict of interest

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Recommended Citation

Ait Ouaissa, Y. Djbrouni, A., Chabani, S., Chabani, M., Amrane, A., Bensmaili, A. (2021). Microwave assisted preparation of onion skin activated carbon: Application for removal of tetracycline.*Algerian Journal of Chemical Engineering*, 01, 16-23.

http://dx.doi.org/10.5281/zenodo.4670571