IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.2 (June 2016) 15- 23
ISSN: 1997-4884

University of Baghdad
College of Engineering

Adsorption of Fluoroquinolones Antibiotics on Activated Carbon by K_2CO_3 with Microwave Assisted Activation

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Abstract

The preparation of low cost activated carbon from date stones and microwave method by using K_2CO_3 as chemical activator were investigated.

The prepared activated carbon was used to remove fluoroquinolones antibiotics from aqueous solution. The characterizations of the activated carbon is represented by surface area, pore volume, ash content, moisture content, bulk density, and iodine number. The adsorbed fluoroquinolones antibiotics are Ciprofloxcin (CIP), Norfloxcin (NOR) and Levofloxcin (LEVO). Different variables as pH, initial concentrations and contact time were studied to show the efficieny of prepared activated carbon. The experimental adsorption data were analyzed by Lungmuir, Freundlich, and Temkin isotherm. The experimental results are described by Lungmiur isotherm. The kinetic data were fitted to pseudo-first order kinetics, pseudo-second order kinetics and interparticle diffusion model. The kinetic adsorption data were best fitted by psuedo-second order kinetic.

Key Words: Date stone, Activated carbon, Microwave, Fluoroquinolones antibiotics, adsorption isotherm, kinetics

Introduction

Fluoroquinolones are synthetic antibiotics; they are a minor group from the major family quinolones. They form a unique group among the bactericidal drugs that used in community sectors, hospitals, and veterinary medicine [1].

Fluoroquinolones have many advantages that enabled them to be ideal antibiotics. They have high potency, good bioavailability, excellent activity against many type of bacteria included gram-positive and gram-negative bacteria, intravenous and oral formulations, low binding and a large distribution volume that made them cross the membranes easily and reach the remote part of human body and low side-effects [2]. Some of fluoroquinolones are used before surgery to prevent inflection; also some of them are studied because they are useful in biliary tract surgery and eye surgery [3-4].

Activated carbon is an excellent adsorbent that is used to remove different organic or inorganic pollutant from many aqueous solutions. Various agriculture wastes or lignocellulose materials such as cotton stalk, date stones, rice husks, apricot stones, olive stones, and almond shell are used to prepare activated carbon [5-8]. The selection of activation method and raw material are important in controlling the physical and chemical characterization of the prepared activated carbon [9-10]. The use of the thermal heating is to enhance surface chemistry and structure of pores [11-12].

Microwave heating is a successful method that is used for preparation and regeneration of activated carbon [13-14]. The microwave would supply energy to the carbon partials. This energy would convert into heat by ionic conduction within the particles themselves. Microwave heating have many advantages such as uniform distribution in temperature, rapid temperature rise, high heating rate, heating process can be controlled easily, reduce the treating time, and saving energy [15-16].

Adsorption is either physical or chemical surface phenomenon in which the concentration of vapor, gas, and liquid accumulate at the contact surface are either undergoing a chemical reaction or not, forming an interface or surface [17]. Adsorption by activated carbon has many advantages over other method as low preparation cost, simple, and free design [18].

The aim of the current work is to study the ability of date stones-carbon for removing the fluoroquinolones antibiotics such as CIP, NOR, and LEVO from solutions. The equilibrium and kinetic adsorption rate are also investigated to understand the mechanism of adsorption.

Material and Method

Material

Date stones were used in this work to prepare the activated carbon. Firstly, the date stones were washed with water to remove the impurities and then dried at 110 °C for 24 h. The date stones were crushed by using disk mill. Finally, the average particle size 1 to 2 mm. K_2CO_3 (provided by Didactic Company, Espuma) with purity of 99.9%, were used as chemical activator for preparation of activated carbon.

The fluoroquinolones antibiotics used are: CIP of purity 99.9% are provided by Nanjing Huaxin Biofarm. Company Ltd., China, NOR with purity 99.9% are provided by Ajanta Pharma Limited Company, India.

Preparation and Characterization

A stainless steel reactor with 3 cm diameter * 15 cm length that was closed in one end and the other end had a removable cover containing a 1mm hole in the middle of it for escaping pyrolysis gases.

Date stones (20g) were put in the reactor and heated in an electrical furnace at 500°C for 1h, then, allowed to cool to room temperature. Each 2 g of the sample above were mixed with 10 ml K_2CO_3 solution with impregnation ratio 0.8 g/g at room temperature for 24 h then they are put in the oven at 110°C until complete drying.

The microwave activation step includes using a quartz reactor 3 cm diameter and 13 cm length. The reactor was closed in on end and the opened to a stainless steel pipe with inside diameter of 5mm. The dried sample was put in the reactor and the reactor put in a microwave oven (MM717CPJ, China) with radiation power 540 W for 8 min radiation time. Then, the sample allowed to cool and socked with 0.1 M HCl solution (10ml/g liquid to solid ratio) for 24 h at room temperature.

Finally, drying sample in the oven at 110 °C for 24 h and weighing the sample to calculate the yield. The prepared activated carbon was stored in desiccator.

The characterizations of activated carbon were represented by surface area, pore volume, ash content, bulk density, moisture content, and iodine number.

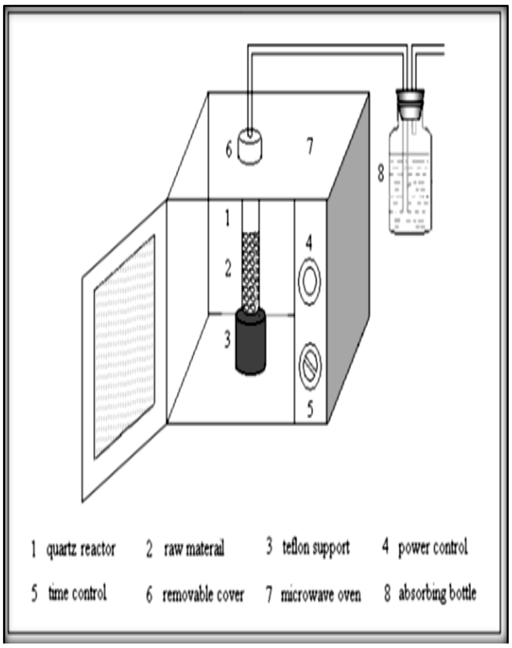

Fig. 1, Schematic diagram of microwave unit for preparation of activated carbon

Adsorptive Removal

The effect of pH, concentration of antibiotics, and contact time were studied by using batch mode adsorption experiment to show the percentage removal of CIP, NOR, and LEVO.

A 0.1 gram of prepared activated carbon with particle size 0.5 to 1 mm was added to 100 ml solution of CIP, NOR, and LEVO with different initial concentration (50 to 200 ppm) and different pH (3 to 11). These mixtures were added to 250 ml flask and shaken at 200 rpm for different periods (15 to120 min). Then, the samples were filtered and the concentrations of antibiotics were measured by using UV-Visible Spectrophotometer at wavelength of 272, 274, and 290 nm for CIP, NOR, and LEVO respectively. The following equation was used to determine the percentage removal of each antibiotic at any time:

$$\text{Percentage Removal } (\%) = \frac{C_o - C(t)}{C_o} * 10 \quad \ldots (1)$$

Where C_o and Ce (mg/l) is the initial and equilibrium concentration of each antibiotics

Adsorption Isotherms

Three important isotherms have been used to correlate the experimental date of CIP, NOR, and LEVO namely Lungmuir, Freundlich, and Temkin [19-20]. Their equations as follows:

$$\text{Lungmuir isotherm} \qquad qe = \frac{ql\ Kl\ Ce}{1+Ks\ Ce} \quad \ldots (2)$$

$$\text{Freundlich isotherm} \qquad qe = Kf\ Ce^{1/n} \quad \ldots (3)$$

$$\text{Temkin isotherm} \qquad qe = B \ln A + B \ln Ce \quad \ldots (4)$$

Where q_l (mg/g) is the maximum adsorption capacity, K_l (L/mg) is the Lungmuir isotherm constant related to the rate of adsorption, K_f ((mg/g) $(L/mg)^{1/n}$) and n is Freundlich constant, related to adsorption capacity and adsorption intensity, respectively. B is the Temkin constant means adsorption heat and A (1/mg) is the constant that related to equilibrium energy.

Adsorption Kinetic

A set of batch mode experiments were carried out to study the effect of contact time on adsorbed amounts of antibiotics to calculate the equilibrium time. The concentration of antibiotics was measured by taking samples of solution at different periods. The adsorbed capacity at time t, qt was calculated by:

$$qt = \frac{(C_o - Ct)V}{W} \quad \ldots (5)$$

Where Ct (mg/l) the concentration of antibiotics at time t (min), mg/l, V (ml) volume of antibiotic solutions, W (mg) weight of activated carbon. Kinetic rates were analyzed with three kinetic models to calculate the rate controlling step and the mechanism of adsorption [21-22]. These models are:

Pseudo-first order model $\ln(qt - qe) = \ln qe - K_1 t$ … (6)

Pseudo-second order model $\frac{t}{qt} = \frac{1}{K_2\, qe} + \frac{t}{qe}$ … (7)

Interparticle diffusion model $qt = K_3\, t^{1/2} + C$ … (8)

Where qe and qt are the uptake of antibiotic at equilibrium and at time t min, respectively, K_1 min^{-1} is the adsorption rate constant, K_2 (mg/g. min) and K_3 (mg/g. $min^{1/2}$) the rate constant of second order and interpartical diffusion respectively, C (mg/g) constant related to the thickness of boundary layer.

Results and Discussions

Yield and Characteristics

The yield and characteristics of prepared activated carbons are listed in Table 1. From this table, the yield is 44% for prepared activated carbon. These results are higher than that found by Haimour and Emeish [23], for activated carbon prepared from date stones activated by phosphoric acid. Their prepared condition 800 °C activation temperature and 0.4 impregnation ratio and 1h activation time. They showed 44% yield. The higher recorded yield of the current results may be due to the use of microwave method that allows activation with lower temperature than 500 °C which reduces the burn off.

Table 1, Characteristics of prepared activated carbon

Characteristics	Value
Surface area, m^2/g	852
Pore volume, cm^3/g	0.671
Ash content, %	3.88
Moisture content, %	4.9
Bulk density, g/ml	0.352
Iodine No.	854.9
Yield, %	44

The surface area and the iodine number are the most important characteristics. The surface area of prepared activated carbon was 852 m^2/g and this result is in agreement with the result of Bamfuleh [24] who reported that the surface area of activated carbon from date stones and zinc chloride activation was in the range of 802 to 1270 m^2/g.

The iodine No. of the activated carbon is 854.9, it's higher than the iodine No. of activated carbon prepared from date stone activated by phosphoric acid 459 that was prepared by Haimour and Emeish [23]. This may be due to the higher micropore content of the activated carbon that prepared by K_2CO_3 of this work.

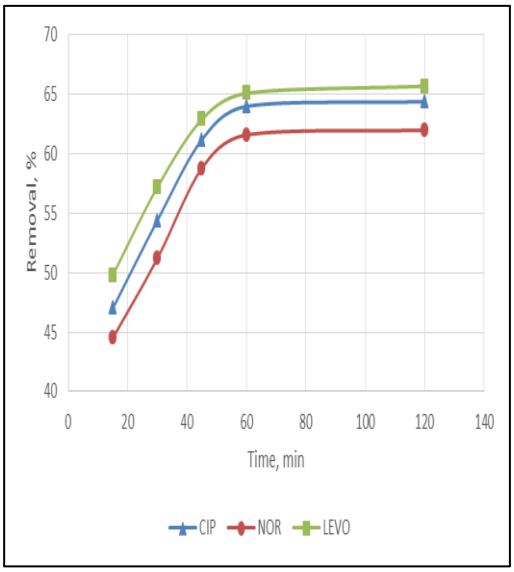

Fig. 2, Effect of time on the removal of CIP, NOR and LEVO

Effect of Time

The effect of contact time on percentage removal of activated carbon on each of fluoroquinolones antibiotics at initial concentration of 150 ppm is shown in Figure 1.

The percentage removal increases with increasing contact time and reaches equilibrium after 90 min. The maximum percentages removal are 64.4, 62 and 65.7 % for CIP, NOR, and LEVO respectively. The percentages removal increases rapidly during the first 45 min, this may be due to the higher driving force which made the transfer of adsorption ions to the particles of activated carbon fast.

Wang et al. [25] and Zhang et al. [26] also showed an equilibrium time of 100 min for antibiotics adsorption on coal fly ash. Ahmed et al. [27] also showed a 90 min equilibrium time for CIP adsorption by albizia lebbeck activated carbon.

Effect of Antibiotics Initial Concentration

The effect of different initial concentration on adsorption capacity of the prepared activated carbon on each type of fluoroquinolones antibiotics for 24 hours is shown in Figure 2. From this figure, it is obvious when the initial concentration increases from 50 ppm to 200 ppm, the adsorption capacity, (qe), increases from 49.28 to 103.06 mg/g, 49.09 to 102 mg/g, and 49.47 to 106.8 mg/g for CIP, NOR, and LEVO, respectively, reach equilibrium at the concentration of 250 ppm. Foo et.al [28] showed an increases in adsorption capacity from 51.06 to 398.45 mg/g when the initial concentration increase from 50 to 500 mg/l.

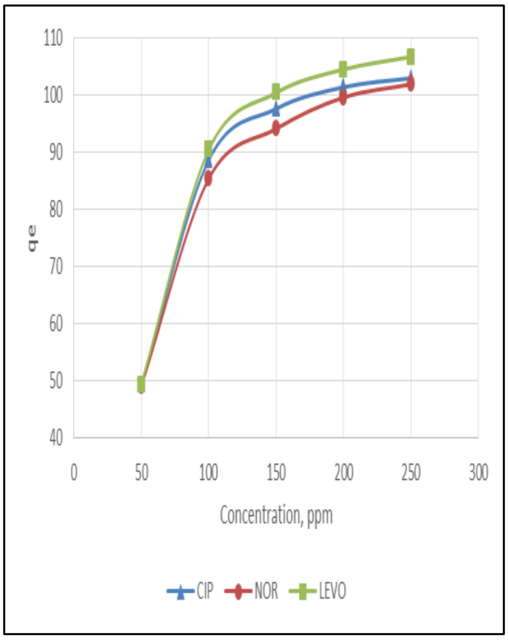

Fig. 3, Effect of the initial concentration of CIP, NOR and LEVO on the adsorption capacity of activated carbon

Effect of pH

In this work different pH from 3 to 11 antibiotic solutions were used to study the percentage removal of each antibiotic on the prepared activated carbon.

Figure 3 shows the effect of different pH at the percentage removal with initial concentration 150 ppm for 24 hours. For CIP and LEVO the maximum percentage removal are 67.9 and 69.8 %, respectively at pH = 9 and percentage removal of 66.4 % at pH=5 for NOR.

Sun et al. [29] and Ahmed et al. [27] considered a pH equal to 8.7 and 9 respectively to be the best pH value for maximum percentage removal for CIP. Liu et.al. [30] showed that the pH= 5.5 is the best value for adsorption of NOR on lotus stalk-activated carbon adsorption.

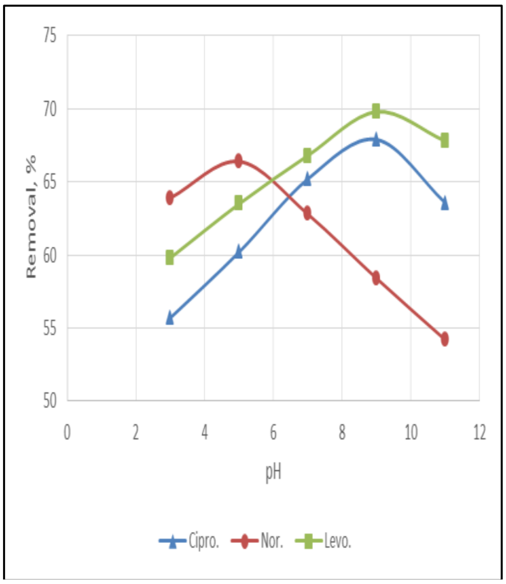

Fig. 4, Effect of pH on the removal of the different antibiotics by activated carbon

Adsorption Isotherm

The three isotherms, Lungmuir, Freundlich, and Temkin isotherms, Eqs. 2, 3, and 4 were used to fit the experimental adsorption data of the three antibiotics. Table 2 shows the calculated constants of the three isotherms with correlation coefficient (R^2) values.

Table 2, Adsorption isotherm parameters for adsorption of the antibiotics by activated carbon

Adsorbate	Lungmuir isotherm		
	qm(mg/g)	K_L (1/mg)	R^2
CIP	101.7	0.01	0.999
NOR	99.71	0.007	0.9989
LEVO	104.76	0.0112	0.9995
Adsorbate	Freundlich isotherm		
	K_F((mg/g)(1/mg)$^{1/n}$)	n	R^2
CIP	1.544	1.371	0.4188
NOR	1.478	1.308	0.4498
LEVO	1.607	1.42	0.3723
Adsorbate	Temkin isotherm		
	A (1/mg)	B	R^2
CIP	1.01	90.53	0.7496
NOR	1.009	87.51	0.7864
LEVO	1.013	92.64	0.717

The highest R^2 values is for Lungmuir isotherm for all three antibiotics with maximum adsorption capacity of 101.7, 99.71 and 104.76 mg/g for CIP, NOR, and LEVO respectively.

This may be explained by that the surfaces of prepared activated carbons have homogenous distribution active sites. Many researchers showed a successful application of Lungmuir isotherm to correlate the experimental data that used for adsorption on activated carbon [31-32].

Adsorption Kinetics

The kinetic data for antibiotic adsorption are fitted to three kinetic models: pseudo-first order model, pseudo-second order model, and interparticle diffusion model (Equations 6 to 8). The results are summarized in Table 3.

The experimental data is better represented by pseudo-second order kinetic model because it gave higher R^2 values while the low R^2 values were for pseudo-first order model. Also for pseudo-first order model a large difference between the calculated and experimental adsorption capacity which indicate a poor model. These results are in agree with several authors who used agricultural precursors to prepare activated carbon for adsorption of antibiotic [30-33].

From Table 3 the lowest R^2 values were obtained for interparticle diffusion model compared with the pseudo-first order and pseudo-second order models. Also large difference between the experimental and calculated data of adsorption capacity.

Table 3, Absorption kinetics of antibiotics over activated carbon

Adsorbate	Pseudo-first order model			
	qe,exp(mg/g)	qe,cal (mg/g)	K1 $(min)^{-1}$	R^2
CIP	97.4	30.144	0.033	0.826
NOR	93.3	31.28	0.034	0.823
LEVO	99.8	25.25	0.028	0.835
Adsorbate	Pseudo-second order model			
	qe,exp(mg/g)	qe,cal (mg/g)	K2(g/mg min)	R^2
CIP	97.4	111.11	0.152	0.998
NOR	93.3	100	0.149	0.998
LEVO	99.8	111.11	0.187	0.999
Adsorbate	Interparticle diffusion model			
	qe,exp(mg/g)	C (mg/g)	K3(mg/g $min^{1/2}$)	R^2
CIP	97.4	62.11	3.626	0.755
NOR	93.3	57.59	3.726	0.757
LEVO	99.8	67.65	3.254	0.75

Conclusions

An activated carbon was prepared by using microwave method and K_2CO_3 as activator and date stones as precursor.

The prepared activated carbon showed an efficient adsorption of fluoroquinolones antibiotics with maximum percentage removal of 64.4, 62.0 and 65.7 % for CIP, NOR, and LEVO respectively. The experimental equilibrium adsorption data were described by Lungmiur isotherm model with maximum adsorption capacity of 101.7, 99.71 and 104.76 mg/g for CIP, NOR, and LEVO respectively. The adsorption kinetic data are represented by pseudo-second order kinetic model.

Abbreviations

Cip	Ciprofloxcin
LEVO	Levofloxcin
NOr	Norfloxcin

Nomenclature

A	Equilibrium energy in Temkin constant, l/mg
B	Adsorption heat in Temkin isotherm.
C	Thickness of boundary layer in interparticle diffusion, mg/g
Ce	Equilibrium condentration of each antibiotics, mg/l
C(t)	concentration of each antibiotics at time t(min), mg/l
C_o	Initial concentration of each antibiotics, mg/l
K_f	Freundlich isotherm constant, $(mg/g).(l/mg)^{1/n}$
K_l	Lungmuir isotherm constant, l/mg
K_1	Adsorption rate constant of pseudo-first order model, 1/min
K_2	Rate constant of pseudo-second order model, mg/g.min
K_3	Rate constant of interpartcle diffusion model, mg/g. $min^{1/2}$
q_e	Uptake of antibiotic at equilibrium, mg/g
q_l	Maximum adsorption capacity, mg/g
q_t	Uptake of antibiotic at time t(min), mg/g
V	Volume of antibiotic solutions, ml
W	Weight of activated carbon, mg

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