

## Batch biosorption removal of total organic carbon from laundry aqueous media using raw pine and acid/microwave irradiation treated pine cone powder

Said Mussa Hafyana<sup>a</sup>, Awad F. Elsheikh<sup>b</sup>, Robert Hausler<sup>a,\*</sup>

<sup>a</sup>Station expérimentale des procédés pilotes en environnement, Ecole de technologie supérieur, 1100, rue Notre-Dame Ouest, Montréal, Que., Canada H3C 1K3, Tel. +1-514-396-8499; Fax: +1-514-396-8584; email: robert.hausler@etsmtl.ca (R. Hausler), Tel. +1-514-701-9589; email: said.hafyana.1@ens.etsmtl.ca (S.M. Hafyana)

<sup>b</sup>Department of Research, Research and Manufacturing Agency, Benghazi, Libya, Tel. +218-92-715-9927; email: awad2003@yahoo.com

Received 16 September 2018; Accepted 14 October 2019

### ABSTRACT

Experimental realization was carried out using available activated carbon pine cone powder (ACPP) as alternative adsorbent for characterized and removal of total organic carbon (TOC) from laundry aqueous solutions, phosphoric acid as an activated factor and microwave as heating source. X-ray diffraction (XRD) spectrum, Fourier-transform infrared spectrometry (FTIR), nitrogen adsorption–desorption isotherms and Brunauer–Emmett–Teller specific surface area and field emission scanning electron microscopy (FESEM) were used to study the surface properties of the ACPP. Using microwave irradiation gives rise to decrease of operation time, savings and homogeneous heating of samples, as opposed to furnace heating. The effects of heat methods,  $H_3PO_4$  concentration, microwave radiation power, microwave radiation time, temperature, initial TOC concentration, ACPP dosage, primary solution pH and soaking time were experimentally studied by batch method to estimate the adsorption capacity, kinetics and equilibrium. The chemical composition of ACPP before and after the modified form is discussed in relation to the XRD, FTIR, SEM and specific surface area results. The results showed that the surface and chemical composition of ACPP samples were modified by  $H_3PO_4$  under microwave radiation are changed after modification. Experimental results showed that the highest removal efficiency and adsorption capacity for removal of TOC took place at basic pH and concentration of 20% of  $H_3PO_4$ . The TOC uptake process obeyed the pseudo-first-order kinetic expression and was best qualified by the Langmuir isotherm. Thermodynamic studies revealed that TOC adsorption on ACPP was exothermic and also spontaneous in nature. The results showed that pine cone could be used as a low-cost alternative for removal of TOC from laundry water.

*Keywords:* Pine cones; Laundry water; Total organic carbon; Adsorption; Alternative biomaterial

### 1. Introduction

Water is an infinite resource, but unfortunately, the concentration of toxic contaminants in water and wastewater has increased due to several industrial processes as well as mining activities [1]. In addition, there is a high level of consumption water such as grey water. The terms ‘diluted’, ‘light’ or ‘grey’ water refer to wastewater produced in residential

areas, from households, office buildings and schools, and industrial wastewater, but it does not include wastewater produced from toilets or any highly contaminated process water. Household wastewater is produced from baths, laundry, and dishwashers and is estimated to represent around 74% of the residential sewage volume [2]. Water that has been used as grey water or household water carries a lot of chemical compounds and chemical pollution. However, if separated from

\* Corresponding author.

black water, grey water can be treated since fewer pollutants are found in laundry water than in grey water [3]. Total volume of laundry water has around one third from grey water [4].

The xenobiotic organic compounds that are probable to be present in grey water represent a heterogeneous group of compounds stemming from household chemicals and personal care products, such as detergents, soaps, shampoos and any cleaning product [1]. The laundry water will include different types of detergents, bleaches and perfumes. As an example, there are at least 900 different organic chemicals compounds and compound groups as detergents found in Danish household products [5].

Therefore, it has an enormous potential to be reused in irrigation because it contains less pollution compared with grey water resulting from kitchen and bathroom [6]. The quality of laundry water differs amongst families, depending on the type of washing machine used, the type of washing powder used, the amount of detergent used and the degree of the soiled clothes that are being washed. Laundry grey water is typically alkaline and it has high sodium concentrations, high levels of phosphorus and high suspended solid concentrations as well as may contain excessive fecal coliforms [3]. The stability and hydraulic characteristics of soils that constantly receive laundry water can be adversely affected by the chemicals present in laundry water, especially sodium [7]. In addition, there are many compounds found in some nitrogen and phosphorous compounds which, mixed with high amounts of organic matter (total organic carbon, TOC), will affect the chemical oxygen demand and biochemical oxygen demand, therefore affecting plant growth by providing delivering plant support, nutrients, water requirement and aeration oxygenation [8]. Thus, removal of TOC from water and wastewater is paramount in protecting the environment [9].

There are physical and chemical methods, which can be used to remove organic matters and compounds from wastewater. Laundry water can be treated by applying a number of different methods [10]. This includes chemical treatment, sedimentation, biological treatment and adsorption [11]. The most widely used method to remove heavy metals and colour is adsorption [12]. Adsorption is a relatively new technique and has gained a great amount of attention since it has shown to be extremely hopeful in the removal of contaminants from effluents in an environmental friendly manner [13]. Bio-sorbents are generally cheap because they are naturally abundant or found as waste material resulting from certain processes. Moreover, adsorption related to carbon chain that has two parts, one as hydrophilic and one as hydrophobic, depends on the surface area [14,15]. The traditional adsorption methods to remove pollutants from water are based on activated carbon and zeolites; also a new alternative with lower costs could use new material, such as pine cones [16,17].

The properties of physical and chemical surface of activated carbon depend on the biomaterial, the method of manufacturing and, more considerably, the heating mechanism [10]. However, the use of conventional heating techniques costs consumption of time, gas, and increases energy so as to keep a relatively high temperature of heated material. Furthermore, carbon will be damaged, as a result of heating and cooling cycles, and requires additional

treatment. Microwave radiation has been effectively utilized for preparation and modification of activated carbons. Reduced processing time and energy consumption, regular temperature, and swift temperature rise are the qualities of this method in comparison with conventional heating methods [10,18]. In terms of health, the use of the microwave radiation ovens is safe whereas the main danger posed is one of proximity. A Federal standard guideline limits the amount of microwaves that can leak from an oven throughout its lifetime to 5 milliwatts (mW) of microwave radiation per square centimeter from the oven surface [19].

The major challenge of this work consists in finding out how to contribute to reduce the amount of TOC in laundry water that is not possible to be reutilized for crop irrigation, due to TOC negative effects on soils. Since total carbon has effect on microscopic soil properties, such as total soil carbon having connection with porosity, saturation percentage, and pore roughness, and because water and solute transport has effect by pore roughness, higher complexity of the pore space leaves more water in the soil, which may increase soil water residence and reduce plant water stress, which means that it can affect the soil structure and crop production [20]. TOC is one of the most significant parameter for the study of water and wastewater quality, because it theoretically concerns all organic compounds. It is about the kinetics of adsorption of TOC from laundry wastewater by using natural and modified bio-material, such as pine cones, as a low-cost alternative adsorbent in the removal of TOC from aqueous solution.

A detailed study on the use of acid/microwave irradiation treated pine cone for removing anionic and organic contaminants has been conducted [10,21,22]. Though, to our knowledge, no studies have been reported relating to the performances of both phosphoric acid ( $H_3PO_4$ ) and microwave irradiation (MW) treated natural pine cone (NPC) for TOC removal from laundry aqueous solutions via batch adsorption.

The main objectives of the present study is to enhance the removal from water of TOC present as soap, using the most cost-effective and efficient process for producing a new low-cost activated carbon pine cone powder (ACPP) as a natural product with chemical agent  $H_3PO_4$  by microwave heating, and to test its efficiency in the removal of TOC using batch experiments. Easy collecting, porous and strong structures are some of the advantages which make pine cone as powerful precursor for the preparation of activated carbon. The effects of pH, temperature, soaking time, initial concentration of detergents (TOC), acid types and concentrations of ACPP dosage were all examined. The NPC and different modified versions of ACPPs were applied in characterization, adsorption, kinetic and isotherms studies.

## 2. Materials and methods

### 2.1. Chemicals and materials

The ACPP used in the experiments was prepared from the NPC of the local area of Mont Royal in Montreal, Quebec, in order to be used as adsorbent to eliminate TOC from laundry water. Table 1 shows the surface functional groups of NPC containing oxygen [13].

Table 1  
Surface functional groups of NPC [13]

Functional groups	mmol g <sup>-1</sup>
Acidic groups	2.958
Carboxylic	1.742
Lactonic	0.723
Phenolic	0.493
Basic groups	1.357

In consistency with the reported methods [13], the raw cones were peeled to remove fiber and center of pine cone, and then thrown out. For clean samples of pine cones, they were washed several times with distilled water, were then dried at 100°C for 24 h in an oven with flipping and rubbing through 24 h.

The dried pine cones were crushed and grounded to obtain a powder. The resultant powder (ACPP) was sieved in British Standards. Sieves and particles between 300 and 400 mm were collected and stored in desiccators for later use as adsorbent material. Phosphoric acid (85.0 wt%, Anahemia Canada Inc.) and sulfuric acid (95.0–98.0 wt%, Fisher Chemical Canada Inc.) have been applied as chemical activating agents. Tide (soap) detergent (Acti-Lift, USA) used as adsorbate and distilled water were the main chemicals used in the experiments.

## 2.2. Equipment

The preparation of the stock solution of commercial washing powders (Tide detergent) was done by dissolving a precisely weighed quantity of the Tide detergent in distilled water. The experimental solutions were prepared by diluting the stock solution with distilled water when necessary to obtain several concentrations. A thermostat shaker (OxiTop IS 12, WTW-R2362) was used for adsorption tests. Also, a microwave oven (Danby designer, Model DMW7700BLDB) was used for preparation of ACPP. Electrical heater (VWR-1305U) was employed to heat samples. The incubator (Rose 1-800-661-9289) was applied for temperatures effect and oven was used as heater, hotplate stirrer (LabTech Germany, Model LMS 1001) was used for the batch experiments. The metal solution was filtered through 0.45 mm membrane filters (Whatman) after settling and was then analyzed using TOC analyzer (TOC APOLLO USA 9000). The pH measurements were performed with a digital ion analyzer and a combination electrode (TitraLab French, TIM 845). The electronic digital thermometer was used to determine the temperature of samples (Fisher Scientific; 50°C–300°C).

## 2.3. Surface modification of NPC with H<sub>3</sub>PO<sub>4</sub> solution/microwave

The NPC (10 g) was soaked with 200 mL varying concentrations of phosphoric acid (10, 20, 40, 60 wt%) in a 300 mL flask for 24 h (soaking time) at room temperature (22°C ± 3°C) with an impregnation char/acid weight ratio of 1:20. Carbonizations of impregnated samples were carried out in microwave oven with power of 700 W (167°C) and radiation times (4 min) under ambient atmosphere. The carbonized samples were placed in an oven at 110°C for 3 h.

Then, samples were washed with distilled water until the pH of washing solution reached 7 ± 0.5, and put overnight in an oven at 60°C for drying. Finally, the obtained activated carbons were finely powdered and stored in desiccators.

To investigate the roles of microwave power and radiation time, vs. electrical heater (E.H) for comparison, 100 mL of commercial washing powders solution (Tide) with a certain concentration (6.45 g L<sup>-1</sup>), TOC concentration 758 ± 0.5 mg L<sup>-1</sup>, was added to 1 g of adsorbents (pine cone) prepared in different conditions. The samples were placed in shaker at 160 rpm and 25°C ± 5°C for 24 h. Then, the adsorbent was separated by filtration and the residual concentrations of TOC were determined with a TOC analyzer.

In order to obtain the ability of prepared carbon for removal of TOC from aqueous solutions, the removal efficiency (%R) was calculated by Eq. (1):

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C<sub>0</sub> is the initial concentration (mg L<sup>-1</sup>) and C<sub>e</sub> is the residual concentration of Tide stock solution after a certain time [10].

## 2.4. TOC adsorption studies

For the prepared ACPP to adsorb TOC, experiment equilibrium and kinetic investigations were done: in the equilibrium adsorption experiments, the adsorption capacity, q<sub>e</sub> (mg g<sup>-1</sup>), which is the amount of TOC adsorbed per unit mass of adsorbent at equilibrium conditions, was derived based on Eq. (2):

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (2)$$

where V (L) is the volume of solution, which was added to the mass of adsorbent, W (g) [10,13,21]. The sorption capacity at time t, q<sub>t</sub> (mg/g) was obtained as Eq. (3):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C<sub>t</sub> (mg L<sup>-1</sup>) was the concentrations of TOC at a given time t [23].

## 2.5. Characterization

NPC and ACPP were subjected to several instrumental characterizations. The X-ray diffraction (XRD) spectra were recorded with a CuKα radiation (λ = 1.5418) at 30 kV and 20 mA ranging from 2θ = 10°–80° and scanning speed of 0.05°/s using a HASKIS TCU 2000/20 (USA). The FTIR spectra of NPC and ACPP were recorded between 400 and 4,000 cm<sup>-1</sup> using a PerkinElmer USA Spectrum, DER LAB USA S000013 model, FT-IR spectrometer Two (Waltham, MA USA). The Brunauer–Emmett–Teller (BET) method, Barrett–Joyner–Halenda (BJH) method and the single point surface area were used to determine the surface area and

the pore diameter distribution of NPC and ACPP by using a Micromeritics Model Tristar 3000 Surface Characterization Analyzer (Atlanta, USA). The samples were degassed by heating them up under continuous  $N_2$  purging. The samples were heated up to  $90^\circ\text{C}$  for 1 h followed by  $120^\circ\text{C}$  for 48 h.  $N_2$  adsorptions were measured at different target pressures under the liquid nitrogen bath and isotherms were obtained for adsorption/desorption. The surface morphologies of NPC and ACPP were examined by a field emission scanning electron microscope using a Hitachi Model SU-8230 SEM (Atlanta, USA).

### 2.6. Adsorption kinetics

The implementation of batch kinetic experiments was carried out by mixing a specific amount of adsorbent (1 g) with 100 mL of Tide soap solution at initial concentration of  $6.45\text{ g L}^{-1}$  in a series of conical flasks. The pH of Tide soap solution was previously adjusted to  $7.00 \pm 0.50$  by adding HCl or NaOH solution. The mixtures were covered and agitated in a shaker at a constant speed of 160 rpm and  $25^\circ\text{C} \pm 5^\circ\text{C}$  for 24 h. After certain duration of stirring, the entire suspension was taken from a conical flask and solid liquid separation was achieved by filtration. The residual TOC concentration in the solution was then determined using a TOC analyzer.

### 2.7. Adsorption isotherms

Isotherm study was conducted using batch equilibrium experiments. Adsorbent 1 g was added into every conical flask with 100 mL of aqueous solution containing different TOC concentrations. TOC solutions were previously adjusted to pH 7.5. The mixtures were shaken at a constant temperature of  $25^\circ\text{C} \pm 0.5^\circ\text{C}$  and a constant agitation rate of 160 rpm using a shaker for 24 h. The mixtures were then filtrated. The residual TOC concentration was finally determined.

### 2.8. Effect of operating conditions onto adsorption of TOC

The adsorption of TOC on NPC and ACPP will be studied by batch technique, our methodological steps being based on the experimental designs based from previous authors who had observed that heat methods [24–26], initial acid concentration, radiation time, radiation power, temperature of  $H_3PO_4$ , initial TOC concentration, biosorbent dosage, soaking time and initial solution pH all play key roles as influential factors on TOC adsorption on ACPP and were investigated by equilibrium experiments in conical flasks. Hence, as to study the heat methods by applying different electrical heat temperatures ( $100^\circ\text{C}$ ,  $250^\circ\text{C}$  and  $550^\circ\text{C}$ ) with different times used for each temperature (2, 4 and 6 h) through constant initial acid concentration (20%), pH ( $6.8 \pm 0.3$ ), TOC concentration ( $758\text{ mg L}^{-1}$ ) and soaking time (24 h) that were used. Also study influence of initial phosphoric acid concentration on removal efficiency of ACPP by 10%, 20%, 40% and 60% with constant microwave power (700W) and microwave temperature ( $167^\circ\text{C}$ ), ACPP dosage of 1 g/100 mL, TOC concentration ( $758\text{ mg L}^{-1}$ ), pH ( $6.8 \pm 0.3$ ), soaking time (24 h) and temperature ( $22^\circ\text{C}$ ) were used. In order to study the

effect of microwave radiation time on the performance of the adsorbent batch, radiation times of 2, 4, 6 and 8 min with contact soaking time of 24 h, constant TOC concentration of  $758\text{ mg L}^{-1}$ , constant pH ( $6.80 \pm 0.3$ ) and constant ACPP dosage of 1 g/100 mL were applied. Also, the effect of microwave radiation power on the effectiveness of the ACPP batch, radiation powers of 400 ( $86^\circ\text{C}$ ), 700W ( $167^\circ\text{C}$ ), 1,100 ( $192^\circ\text{C}$ ) and 1,600 W ( $284^\circ\text{C}$ ) with contact radiation time of 4 min, constant TOC concentration of  $758\text{ mg L}^{-1}$ , contact soaking time of 24 h, constant pH ( $6.8 \pm 0.3$ ) and constant ACPP dosage of 1 g/100 mL were applied. The effect of the impact of temperature of the laundry aqueous solution on the act of the ACPP was studied using incubator at  $12^\circ\text{C}$ ,  $22^\circ\text{C}$ ,  $37^\circ\text{C}$  and  $50^\circ\text{C}$  with constant TOC concentration of  $758\text{ mg L}^{-1}$  (Tide soap concentration of  $6.45\text{ g L}^{-1}$ ), constant initial acid concentration (20 wt%), contact soaking time of 24 h, constant pH ( $6.8 \pm 0.3$ ) and constant ACPP dosage of 1 g/100 mL were applied. The impact of adsorbent (pine cone) dosage on the performance of the ACPP was studied using various weights of 500, 750, 1,000 and 1,200 mg with constant TOC concentration of  $758\text{ mg L}^{-1}$  (Tide soap concentration of  $6.45\text{ g L}^{-1}$ ) and constant initial acid concentration (20 wt%). So, as to study the effect of initial concentration of TOC on effectiveness of ACPP, used varied concentrations of TOC at 488, 758, 969 and  $1,284\text{ mg L}^{-1}$  (equivalent to 4.45, 6.45, 8.45 and  $10.45\text{ g L}^{-1}$  of Tide soap concentration, respectively) with constant time irradiation of 4 min, constant ACPP dosage of 1 g, constant initial acid concentration (20 wt%), contact soaking time of 24 h, constant pH ( $6.8 \pm 0.3$ ) and temperature of  $22^\circ\text{C} \pm 3^\circ\text{C}$ . Moreover, the effect of soaking time on the act of the ACPP was studied using 6, 12, 18 and 24 h with constant ACPP dosage of 1 g and constant time irradiation of 4 min. Also, for initial pH effect study at same constant conditions, initial TOC concentration was  $758\text{ mg L}^{-1}$ , ACPP dosage 1 g and Tide soap solutions were adjusted to pH 4.00, 7.00, 10.00 and  $12.00 \pm 0.3$ . Effluent samples from the batch were collected at specified time intervals, and remaining TOC concentrations in the solution taken from conical flasks, and solid-liquid separation achieved by filtration, were determined by a TOC analyzer. The obtained results for measured the first value of total carbon (TC) then moved the inorganic carbon (IC) from first value by using  $H_3PO_4$  and Azote gas until reaching a value of pH = 2 or less; after that, measured (TC) as a second value by the device, in this case:  $\text{TC} = \text{TOC} + \text{IC}$ . However, when (IC) was removed and the sample measured, it became:  $\text{TC} = \text{TOC}$  [27]. In all experiments, the temperature value was controlled to  $25^\circ\text{C} \pm 0.5^\circ\text{C}$ . The pH of TOC solution was  $7.00 \pm 0.10$  adjusted to a given value by adding either HCl or NaOH to study the effect of pH on TOC solution.

## 3. Results and discussion

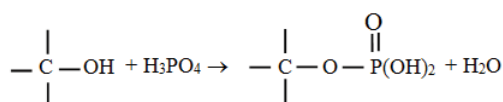
### 3.1. Determination of optimization active carbon pine powder

The removal of TOC by NPC and ACPP samples at different phosphoric acid initial concentrations (10–60 wt%) was studied using microwave and electrical heater (E.H) as shown in Table 2. The experimental results indicated that all ACPP which used microwave irradiation with phosphoric acid showed great enhanced removal efficiency of TOC compared with NPC and NPC-E.H. The concentration of

TOC adsorbed onto ACPP is directly related to the percentage loading of  $H_3PO_4$  adsorbed on NPC. The optimum acid concentration of ACPP by  $H_3PO_4$  occurred at 20 wt% (ACPP-20%), a value that has been previously used in characterization and then later used in kinetic and modeling studies of ACPP-20%. The ACPP-20% exhibited the highest removal efficiency (%R) and adsorption capacity ( $q_e$ ) of TOC among other modifying samples.

This may be attributed to two reasons: Microwave irradiation is a key factor that can have an effect on adsorption capacity and removal efficiency [10,28,29]. The heat methods of NPC by microwave with phosphoric acid lead to a rising adsorption of TOC which covered the pine cone surface (ACPP), thus, allowing an increase in the adsorption capacity of pine cone. Whereas, applying electrical heat causes the carbon and porous structures to become damaged, also as a result of external heating that does not give a homogeneous temperature for different shapes and sizes of NPC. Therefore, the NPC-E.H did not show any removal for TOC. Microwave radiation has been successfully implemented to the production and modification of activated carbon. It can be concluded that, due to high heating speed and direct energy contact with the carbon layer, activated carbon porosity has been arisen effectively [10,22].

On other hand, Table 2 also reveals that ACPP was affected by  $H_3PO_4$  concentration, with the optimum adsorption for ACPP being attained by 20 wt%. Above the  $H_3PO_4$  concentration level of 20%, the reduced volume was effectively reduced to adsorption due to large molecules of TOC. Table 2 illustrates dependency of removal percentage of TOC by the prepared ACPP with different acid initial concentrations (20–60 wt%). Depending on reaction which is exposed below, throughout activation of NPC,  $H_3PO_4$  molecules could be altered into polyphosphoric acid and water, which may produce a reaction with the OH functional groups present on the surface of NPC [10].



As can be seen in Table 2, increasing acid concentration from 10 to 20 wt% improves the chemical activation reaction and become successfully complete. In addition, the removal efficiency and adsorption capacity of TOC was enhanced with the increase of acid concentration from 10 to 20 wt%. Increased acid weight percentage leads to increase of total surface area, pore volume, mesoporous area and other structures [22].

In contrast, fine powder that was entered into pores can be removed by a diluted solution of  $H_3PO_4$  (20 wt%), and be blocked, which facilitates pore access. An increase in initial concentration of acid from 20 to 60 wt% show increased removal efficiency while adsorption capacity is found to have negligible decrease. Thus, increasing  $H_3PO_4$  has no effect on the kinetics of the reaction between precursors and the activating agent [10]. Then, removal efficiency was decreased slowly with the increase of  $H_3PO_4$  concentration from 40 to 60 wt%. Thus, because of severe oxidation, structure of NPC was damaged and adsorption capacity was decreased. Moreover, excessive acid concentration blocked the pores and insulation layer could be shaped.

The described adsorption pattern may explain why the best performance took place with an acid concentration equal to 20 wt%. Based on Table 2, the removal efficiency (%R) and adsorption capacity ( $q_e$ ,  $mg\ g^{-1}$ ) of ACPP are highest for ACPP-20%, that is, almost 73.480% and 55.700  $mg\ g^{-1}$ , respectively, higher than that of NPC and ACPP-EH [10].

### 3.2. Characterization of NPC and ACPP

The treatment pine cones used for the characterizations, NPC-E.H550 and ACPP-20%, were prepared under the following conditions: microwave power of 700 W, temperature of 167°C, radiation time 4 min and phosphoric acid at 20% for electrical heat activation; electrical heat temperatures 550°C, phosphoric acid 20% and activation time 2, 4 and 6 h for thermal activation. The pine cone was milled into powder for its XPS, FTIR, SEM and EDS, surface area and pore analysis.

#### 3.2.1. Structural characterization by XRD technique

The X-ray diffractograms were used to determine the crystallographic structures of the NPC, NPC-E.H550 and

Table 2  
Comparison of removal efficiency of TOC of samples prepared

Sample	Method of heat		Acid concentration (wt%)	Yield (wt%)	%R	$q_e$ ( $mg\ g^{-1}$ )
	MW (W)	EH (°C)				
NPC	–	–	–	86	0.000	0.000
NPC-20%	–	–	20	81	0.000	0.000
NPC-E.H100	–	100	20	53	0.000	0.000
NPC-E.H250	–	250	20	44	0.000	0.000
NPC-E.H550	–	550	20	39	0.000	0.000
NPC	700	–	–	67	0.000	0.000
ACPP-10%	700	–	10	64	51.720	39.200
ACPP-20%	700	–	20	68	73.480	55.700
ACPP-40%	700	–	40	70	34.790	26.500
ACPP-60%	700	–	60	66	32.330	25.100

ACPP at different conditions as presented in Fig. 1. Powder X-ray pattern of the samples was recorded over at  $2\theta = 10^\circ$ – $90^\circ$  range. All of the samples before and after treatment (NPC, NPC-E.H550 and ACPP-20%) show well-defined crystalline peak of cellulose and do not exhibit sharp crystalline peaks due to the amorphous nature [30]. Compared with the spectrum of untreated powder, those of the NPC-E.H550 and ACPP-20% demonstrated a decrease in intensity and broadening of the peaks after treated. The spectra detected that NPC is composed mainly of crystalline cellulose as indicated by the peak at  $2\theta = 25.55^\circ$  [31].

XRD patterns indicate that all samples have partially disordered crystal structure (Fig. 1) [32]. NPC sample consisting of two relatively strong broad peaks at  $16.89^\circ$  and  $25.87^\circ$  and another sharp weak broad peak at  $32.50^\circ$ . The spectrum of treated samples shows ACPP-20% corresponding more to NPC than to NPC-E.H550 sample, with ACPP-20% sample consisting of one relatively strong broad peak at  $25.53^\circ$  and one weak broad peak at  $32.50^\circ$ , whereas NPC-E.H550 sample consists of one very strong broad peaks at  $5.02^\circ$  with two other strong broad peaks at  $12.04^\circ$  and  $25.87^\circ$  as well as a weak broad peak at  $50.74^\circ$ . It is obvious that the strong and weak broad peaks slightly move to higher angles as carbonization temperature are increasing. However, it moves more for NPC-E.H550 than ACPP-20% due to the effect of higher temperature on the crystalline structure of NPC, which in turn affects the effectiveness of TOC removal.

### 3.2.2. FTIR spectroscopy

The FTIR spectra can provide valuable information about the chemical compositions of the materials. Fig. 2 demonstrates the FTIR spectra of NPC, NPC-E.H550 and ACPP-20%. It was shown that the NPC contained much more bands than the modified pine cones. However, the NPC-E.H550 has fewer bands compared with ACPP-20% as a result of being exposed to heat. The wave number range of FTIR spectrum is from 400 to  $4,000\text{ cm}^{-1}$ . Fig. 2 shows that the NPC before treatment has a wide absorption band at  $3,093$ – $3,637\text{ cm}^{-1}$ , with a maximum at about  $3,377\text{ cm}^{-1}$  assigned to O–H stretching vibrations of hydrogen-bonded hydroxyl groups [16].

A peak around  $1,682\text{ cm}^{-1}$  can be attributed to C=O stretching vibrations of ketones, aldehydes, lactones or carboxyl groups [13]. Also bands which can be seen at around

$1,557\text{ cm}^{-1}$  are related to COO– group on NPC [33]. Aliphatic C–H stretching vibration is found as a very soft peak at  $2,867\text{ cm}^{-1}$ , whilst asymmetric vibration of  $\text{CH}_2$  group shows at  $2,940\text{ cm}^{-1}$ . The peaks around  $1,029\text{ cm}^{-1}$  probabilities are assigned to the –C–C– [34]. As for the modified pine cones, NPC-E.H550 and ACPP-20%, they have a new wide absorption band at around  $1,570\text{ cm}^{-1}$  which may have originated from the use of phosphoric acid (P=O). Likewise, pine cone material treated with  $\text{H}_3\text{PO}_4$  exhibited a significantly increased carboxyl group fraction but the effect of temperature of electrical heater on structure of NPC led to no adsorption capacity of TOC, unlike the pine cone treated by microwave use.

### 3.2.3. SEM-EDS analysis

The surface features of the three study materials were examined by SEM-EDS analysis of various magnifications to determine the micro-structure and elemental composition of NPC, NPC-E.H550 and ACPP-20%, which are illustrated in Fig. 3. The surface of the NPC sample was smooth and uneven, with small visible waves that may be caused by the carboxylic groups and other extracts (Fig. 3a). SEM illustrates that the average pore sizes of NPC are very small ( $0.034\text{ mm}$ ). After treatment, Fig. 3b for NPC-E.H550 shows more roughness surface with cracks and the absence of small waves, which may be as a result of the electrical heater's temperature effect on pine cone structure among with noticeable increased the average pore size [10,28,29]. The smooth edges surface of the ACPP-20%, which is almost similar to NPC, is an indication that phosphoric acid was coated on the surface of the pine cone and microwaves radiation did not affect too much on the pine cone surface, as showed in Fig. 3c. Consequently, the average pore sizes also increased more than with other samples ( $63\text{ mm}$ ).

EDS detected the emission of elements of carbon (C) and oxygen (O). Fig. 3a demonstrates the percentage (wt%) of all elements before adding phosphoric acid, as per the following order: C (38.81%) < O (61.19%). Similarly, the percentage (wt%) of all elements present in NPC-E.H550 and ACPP-20%, which included  $\text{H}_3\text{PO}_4$ , was investigated as per the following order: C (8.43, 8.21%) < O (10.74, 12.33%) < P (5.11,

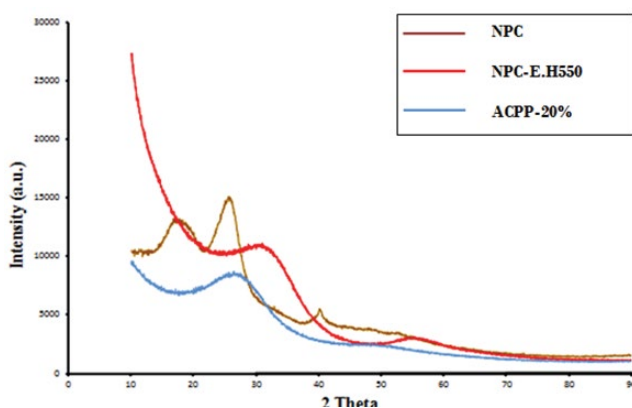


Fig. 1. XRD patterns of NPC, NPC-E.H550 and ACPP-20%.

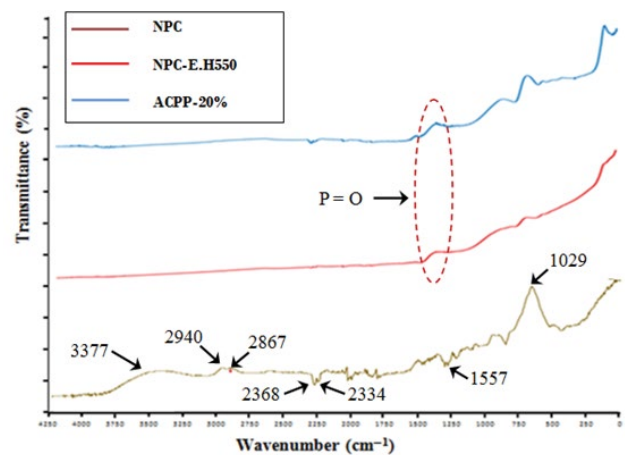


Fig. 2. FTIR spectrum of NPC, NPC-E.H550 and ACPP-20%.



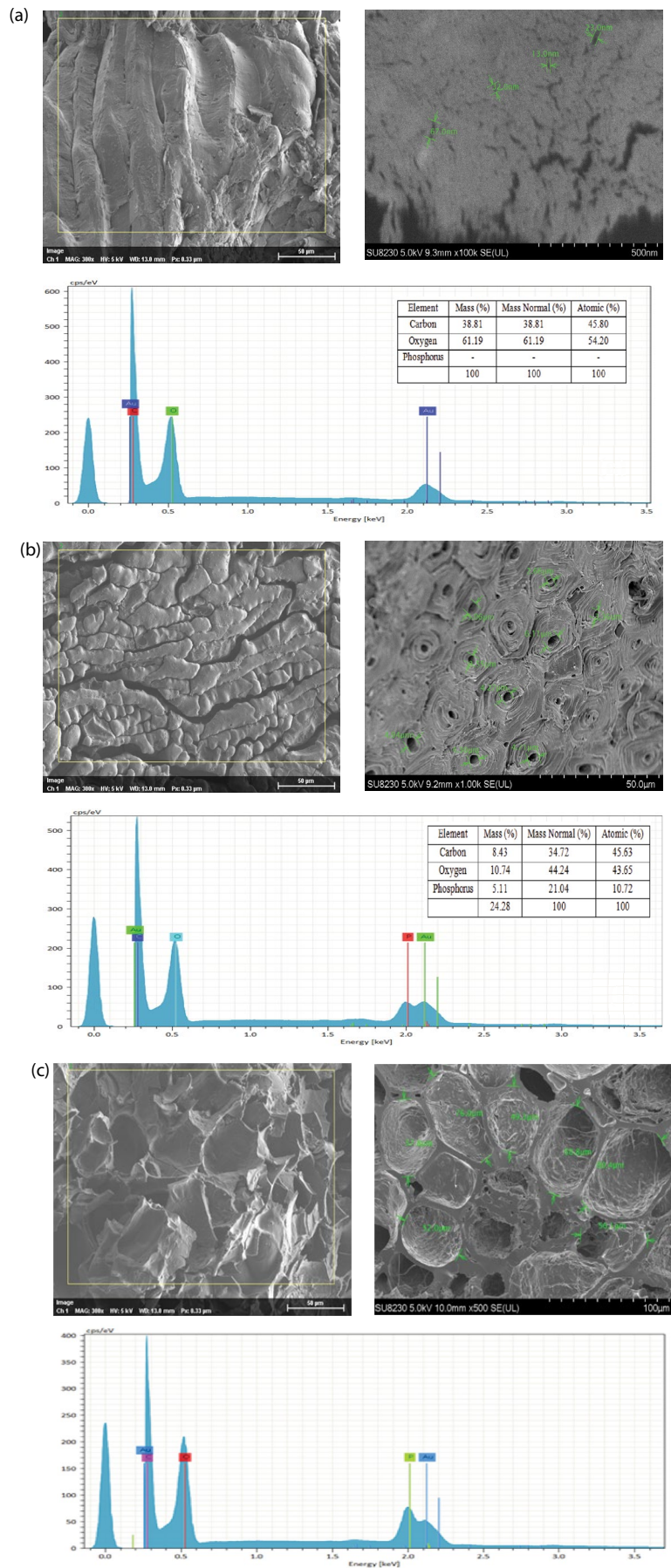


Fig. 3. SEM-EDS analysis of (a) NPC, (b) NPC-E.H550 and (c) ACP-20%.

7.33%), respectively (Figs. 3b and c). Thus, pine cones treated activation by microwave radiation with  $H_3PO_4$  exposed increased carbon and oxygen content, as well as phosphorus, compared to NPC-E.H550. These results reported that the presence of fractions of oxygenated functional groups, such as carboxylic and phenolic groups, were developed on the adsorbent with higher average pore sizes, which may have contributed to increasing TOC adsorption [35].

### 3.2.4. Surface area and pore analysis

The surface area and porous properties of the pine cone samples were further investigated using the nitrogen adsorption–desorption isotherm. One of the most significant properties which brought about activated carbons, known as a recognized and powerful adsorbent, is their adsorptive capacity which is related to pore size, pore distributions and specific surface area [10,36]. Table 3 shows the surface area of NPC, NPC-E.H550 and ACP-20% samples by single-point surface area at the relative pressure ( $P/P_0$ ) = 0.22, BET and Langmuir, as well as lists the porosity details of samples. The  $N_2$  adsorption–desorption isotherm plots and BJH pore diameter distributions of NPC, NPC-E.H550 and ACP-20% samples are presented in Figs. 4–6, respectively.

The results shown in Table 3 reveal that NPC sample powder had the least value of surface area (single point =  $0.1015 \text{ m}^2 \text{ g}^{-1}$ , BET =  $0.1005 \text{ m}^2 \text{ g}^{-1}$  and Langmuir =  $0.1358 \text{ m}^2 \text{ g}^{-1}$ ), even though this value is smaller than that measured for raw pine cone ( $4.39 \text{ m}^2 \text{ g}^{-1}$ ) as reported by Ofomaja et al. [16] also ( $569 \text{ m}^2 \text{ g}^{-1}$ ) as reported by Karthikeyan et al. [37]. Also, NPC sample had the least value pore volume and pore size. Classic thermal heating of activated carbon after consecutive treatment and recovery cycles in an electrical furnace reduce the adsorption capacity considerably, which is credited to the adverse changes in the adsorbent physical structure [38]. Therefore, the modified sample NPC-E.H550 had a large surface area, pore volume and smaller pore size but did not show the ability to adsorption of TOC (Table 2). Otherwise, the modified sample ACP-20% demonstrates the most value of surface area, pore volume and small pore size, so it shows great ability to adsorption capacity as a result of microwave radiation effect and packing density of  $H_3PO_4$  (Table 2). Furthermore, in comparison with other NPC-E.H550 samples, the ACP-20% sample possessed a high number of functional groups (Fig. 3) [39]. The surface area and pore volume results follow the trend: NPC > NPC-E.H550 > ACP-20%. The increase in surface area causes a better adsorption capacity and this is in agreement with the XRD, SEM-EDS results. In contrast,

Table 3  
Surface area and porosity details of NPC, NPC-E.H550 and ACP-20%

Pine cone	NPC	NPC-E.H550	ACPP-20%
Surface area ( $\text{m}^2 \text{ g}^{-1}$ )			
Single point	0.1015	117.5978	206.1723
BET	0.1005	119.6046	212.8340
Langmuir	0.1358	150.6608	291.9043
Pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )			
BJH adsorption	0.004585	0.016382	0.082271
BJH desorption	0.004586	0.014066	0.079131
Pore size ( $\text{\AA}$ )			
Adsorption average pore width	117.444	17.680	21.981
BJH adsorption	1,256.977	39.897	37.068
BJH desorption	1,135.374	42.389	37.208

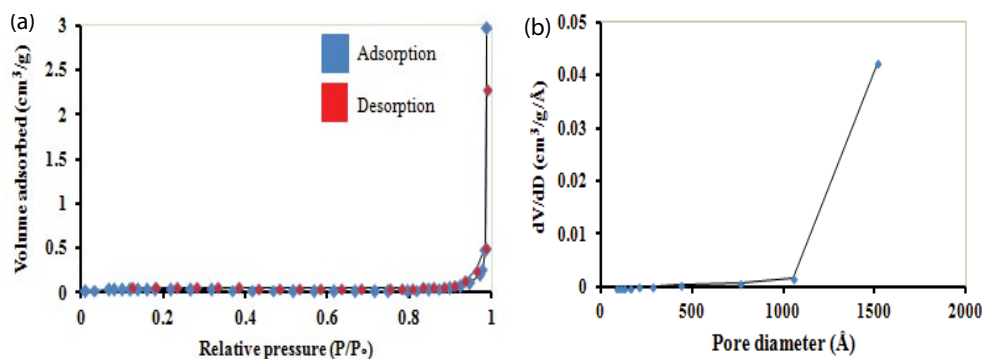


Fig. 4. (a)  $N_2$  adsorption–desorption isotherms and (b) BJH pore diameter distributions of sample NPC.



NPC had only macropores, other than that after different modifications, NPC-E.H550 and ACP-20%, a microporous and mesoporous structure could be formed, respectively.

On the other hand, Figs. 4a, 5a and 6a, respectively, show the  $N_2$  adsorption–desorption isotherm with the evident hysteresis phenomenon and the pore-size distribution of the pine cone samples [40]. These isotherms can be classified as Type II for NPC sample with macroporous and Type I for NPC-E.H550 sample with microporous; whereas, ACP-20% sample illustrates Type IV with a distinct hysteresis loop observed in the range of 0.5–1.0  $P/P_0$ , which improves the presence of mesopores in all ACP-20% samples [10,41]. The data are listed in Table 3.

Otherwise, according to the IUPAC recommendations, the hysteresis loops for NPC sample are Type H1 loops and show parallel and nearly vertical branches (Fig. 4a). This type of hysteresis loop was frequently reported for materials that consisted of agglomerates or compacts of approximately spherical particles arranged in a fairly uniform way. In addition, it has become clear that H1 hysteresis loops are also a characteristic of materials with cylindrical pore geometry and a high degree of pore size uniformity. Therefore, the presence of the H1 hysteresis loop on the adsorption isotherm for a porous solid usually indicates its relatively high pore size uniformity and facile pore connectivity [39,41,42]. The NPC-E.H550 sample (Fig. 5a) confirms the hysteresis of Type H3 loop that do not level off at relative pressures close to the saturation vapor pressure were reported for materials comprised of aggregates of plate-like

particles forming slit-like pores. Type H3 loop exhibiting triangular shape with an almost horizontal desorption branch that falls steeply close to the lower limit of adsorption–desorption hysteresis may be indicative of the presence of disordered structures [39,41,42]. Fig. 6a demonstrates the ACP-20% sample is of Type H4 hysteresis loops (Fig. 6a) and may only be produced from the existence of big mesopores. Type H4 loops feature parallel and nearly horizontal branches and their appearance has been due to adsorption–desorption in narrow slit-like pores. Specifically, Type H4 loop that showed particles with internal voids of irregular shape and broad size distribution [39,41,42]. These analyses agreed well with BJH pore diameter distributions of pine cone (Figs. 4b, 5b and 6b), which confirmed that the NPC and ACP-20% have a wide pore diameter distribution in macroporous and mesoporous domains while NPC-E.H550 had a narrow pore diameter distribution in microporous domains. Overall, based on all results of surface area and porosity details, it was found that the surface area and pore volume increased after modification, while pore size decreased. This is part of the main reasons that enabled the ACP-20% to have enhanced adsorption capacity for TOC compared with NPC and NPC-E.H550.

### 3.3. Influence of operating conditions on adsorption of TOC

#### 3.3.1. Effect of microwave radiation time

Microwave radiation time plays an important role in carbon quality, affecting removal efficiency and adsorption

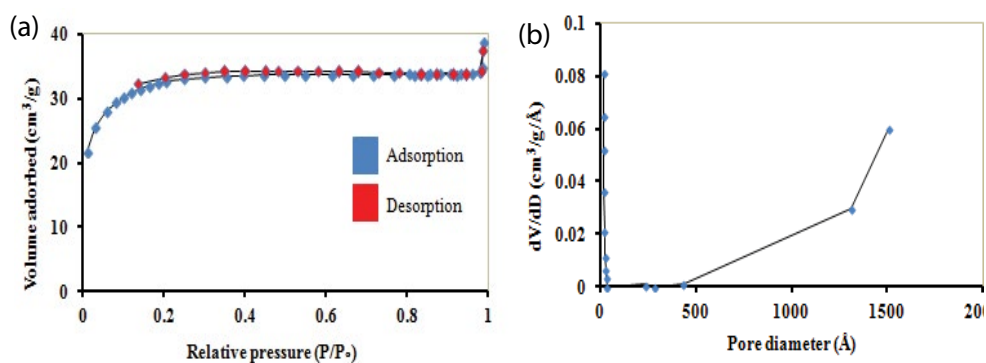


Fig. 5. (a)  $N_2$  adsorption–desorption isotherms and (b) BJH pore diameter distributions of sample NPC-E.H550.

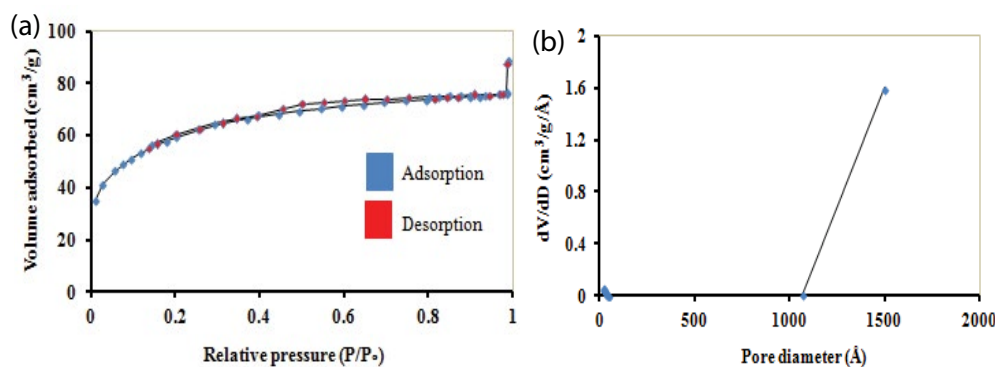


Fig. 6. (a)  $N_2$  adsorption–desorption isotherms and (b) BJH pore diameter distributions of sample ACP-20%.

capacity. Effects of microwave radiation time on adsorption capacity were evaluated at microwave power level 700 W. Fig. 7 shows that extending radiation time from 2 to 4 min caused an increase in removal efficiency and adsorption capacity from 48.020% to 73.480% and from 36.200 to 55.700 mg g<sup>-1</sup>, respectively.

It can be concluded that the pores structures of pine cone are affected by extending radiation time. Thus as the radiation time achieves its optimum time, removal efficiency reaches its maximum value. As indicated by these results, removal efficiency remains relatively increase then has a considerable decrease. This is since the degree of activation depends more on microwave radiation time than on the activation agents' concentration [43]. The probable explanation was that increased radiation time caused the samples to get higher energy. When microwave radiation time reached a certain level (as in this study, radiation time > 4 min), overfull energy could break C–O–C and C–C bonds, burn carbon structures and damage the pores. Subsequently, decreased surface area and removal efficiency is expectable [10,22].

### 3.3.2. Effect of microwave radiation power

Microwave radiation power is a key parameter which can affect removal efficiency and adsorption capacity [10]. The results which are presented in Fig. 8, indicate the variation of TOC removal percentage by microwave radiation power used for ACP-20%. The results expose that pore structures were not adequately developed under low microwave radiation power level of 400 W (86°C), but with increase of microwave power, removal efficiency also increased gradually from 15.72% to 75.6%. At the same time, it was observed that the adsorption capacity decreased from 55.70 to 47.6 mg g<sup>-1</sup>. It can be deduced that, due to high heating speed and energy direct contact with the carbon bed, porosity of activated carbon was effectively increased at radiation power 700 W [10,29]. Another possible explanation is that the effect of microwave radiation power is only relevant to the pine cone structure, where increased heating radiation lead to increased pore size but decreased surface area. Consequently, removal efficiency will be greater than before and adsorption capacity lesser. The assumption

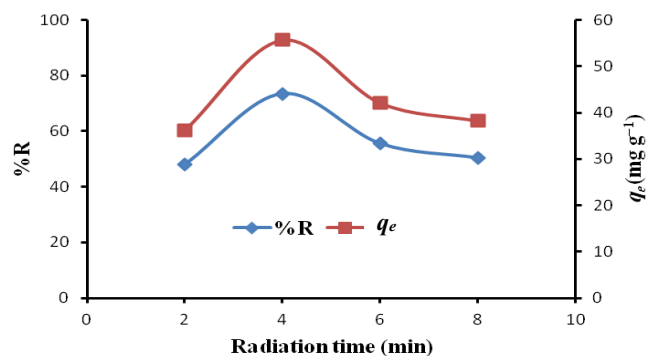


Fig. 7. Effects of microwave radiation time on removal efficiency and adsorption capacity of ACP-20% for removal of TOC (758 mg L<sup>-1</sup>) from aqueous solution, acid concentration 20 wt%, saturation time 24 h, pH = 10.

is that the appropriate microwave radiation power which determines the homogeneity of the ACP-20% in this study was 700 W.

### 3.3.3. Effect of temperature

The investigation of temperature revealed a significant effect on the operation of ACP-20%, as the removal efficiency and adsorption capacity of TOC in aqueous media was studied at four various temperatures (Fig. 9).

Temperature is shown to be an indicator for the adsorption nature, whether it is an exothermic or endothermic process [16,21]. The results demonstrated that the removal efficiency and adsorption capacity are 73.750; 55.90, 73.480; 55.700, 69.530; 52.700 and 64.910; 49.200 at 12°C, 22°C, 37°C and 50°C, respectively. There is an inverse relationship between removal of TOC and temperature. Fig. 9 shows that the amount of TOC adsorption on ACP-20% increased with the decreasing temperature of the soap solution, which indicates that the process was exothermic. The adsorption capacity increased with the decreasing temperature, indicating that the adsorption is an exothermic process [20]. The fact that the percentage of TOC removal is favored at lower temperature

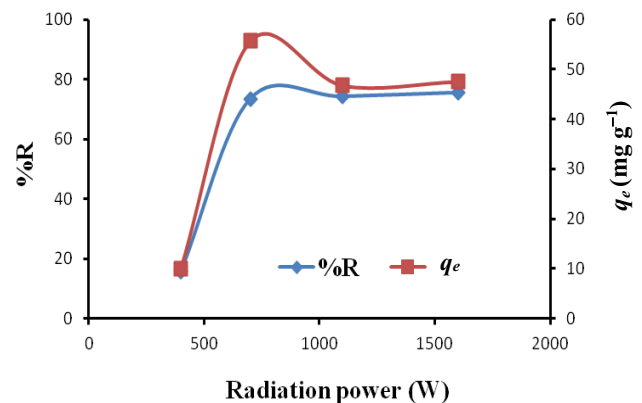


Fig. 8. Effects of microwave radiation power on removal efficiency and adsorption capacity of ACP-20% for removal of TOC (758 mg L<sup>-1</sup>) from aqueous solution, acid concentration 20 wt%, irradiation time 4 min, pH = 10.

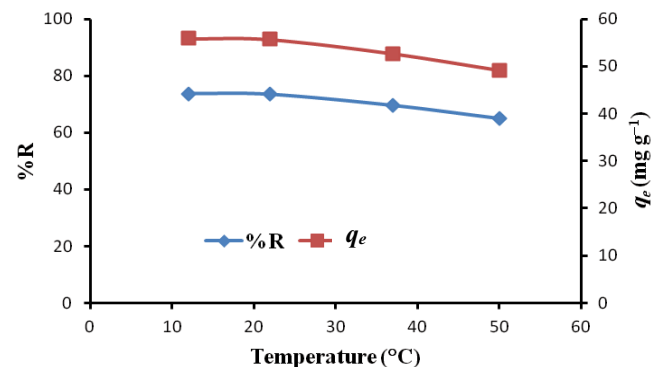


Fig. 9. Effects of temperature of H<sub>3</sub>PO<sub>4</sub> on removal efficiency and adsorption capacity of ACP-20% for removal of TOC (758 mg L<sup>-1</sup>) from aqueous solution, acid concentration 20 wt%, irradiation time 4 min, pH = 10.

indicates that the mobility of the TOC ions decreases with a rise in the temperature. It can also be said that decreased temperature of reaction enhances the reaction of TOC and surface functional groups.

### 3.3.4. Effect of initial TOC concentration

The initial TOC concentration has a pronounced effect on its removal from aqueous solutions. The effect of initial TOC concentration onto ACP-20% adsorbent was investigated and the results are presented in Fig. 10. It was also found that the amount of adsorption, that is, mg of adsorbate per g of adsorbent, increases with decreasing removal efficiency at all initial TOC concentrations, and that equilibrium is attained at 969 mg L<sup>-1</sup>. This is so because the initial TOC concentration provides the driving force to overcome the resistance to the mass transfer of TOC between the aqueous solution and the solid phase.

For constant dosage of ACP-20%, at higher initial TOC concentration, the available adsorption sites of ACP-20% become fewer and hence the removal efficiency of TOC depends upon the initial TOC concentration [21]. The increase in initial TOC concentration also improves the interaction between ACP-20% and TOC. Therefore, an increase in initial TOC concentration leads to enhanced adsorption uptake of TOC.

### 3.3.5. Effect of biosorbent dosages

The study of ACP impact at 20% dosage demonstrates an adsorbent's efficiency and a TOC's ability to be adsorbed with a minimum dosage, allowing determining a TOC's ability from an economical standpoint [21]. Varying the ACP-20% dosage for a fixed volume (100 mL) of Tide detergent solution at constant concentration (6.45 g L<sup>-1</sup>) has an effect, as shown in Fig. 11.

It is observed from Fig. 11 that increasing the ACP dose increased the percentage of TOC removal from aqueous solution, from 58.310% to 83.910%. On the other hand, the amount of TOC adsorbed per unit mass of ACP was also found to increase with biosorbents dose from 44.200 to 63.600 mg g<sup>-1</sup> (Fig. 11). It is obvious that, by increasing the dose of the

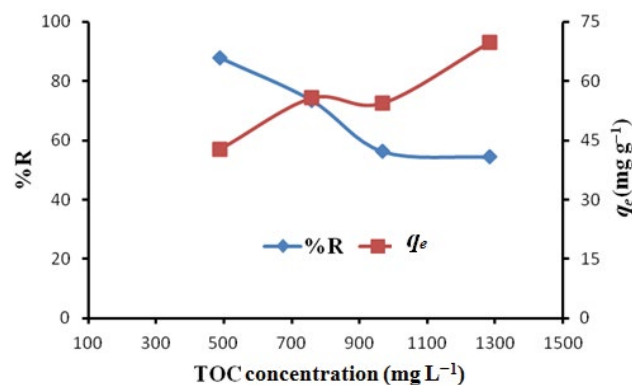


Fig. 10. Effects of initial TOC concentration on removal efficiency and adsorption capacity of ACP-20% for removal of TOC from aqueous solution, acid concentration 20 wt%, irradiation time 4 min, pH 10.

ACPP-20%, the number of sorption sites obtainable for sorbent-solute interaction is increased, thereby resulting in the increased percentage of TOC removal from aqueous solution [16,21].

### 3.3.6. Effect of soaking time

Soaking time of NPC by phosphoric acid plays a decisive role in carbon quality, affecting adsorption and removal efficiency. Effects of soaking time on adsorption capacity were evaluated under microwave power level of 700 W, TOC concentration of 758 mg L<sup>-1</sup>, with increasing soaking times of 6, 12, 18 and 24 h. Fig. 12 indicates that soaking time from 6 to 12 h caused a decrease in removal efficiency and adsorption capacity from 82.320%; 62.400 mg g<sup>-1</sup> to 73.480%; 55.700 mg g<sup>-1</sup>, respectively. It can be deduced that increased soaking time leads to packing porosity by acid, so the pore size decrease causes reduced adsorption capacity and removal efficiency [10,44,45].

However, as the soaking time achieves its optimum time, removal efficiency and adsorption capacity reach its maximum value. These results suggest that removal efficiency

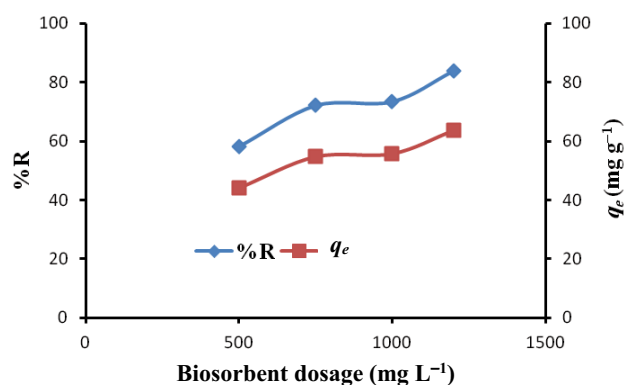


Fig. 11. Effects of biosorbent dosage on removal efficiency and adsorption capacity of ACP-20% for removal of TOC (758 mg L<sup>-1</sup>) from aqueous solution, acid concentration 20 wt%, irradiation time 4 min, pH 10.

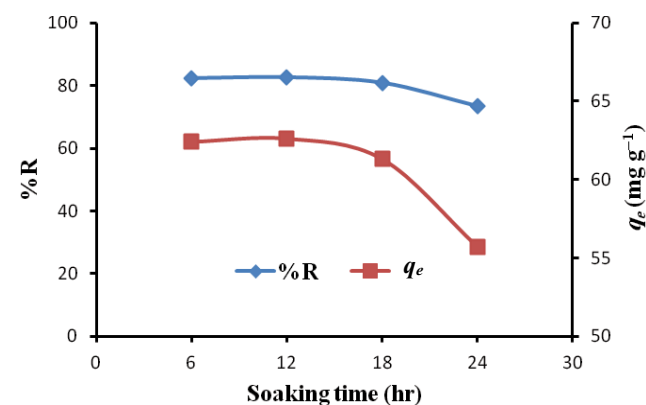


Fig. 12. Effects of soaking time on removal efficiency and adsorption capacity of ACP-20% for removal of TOC (758 mg L<sup>-1</sup>) from aqueous solution, acid concentration 20 wt%, irradiation time 4 min, pH = 10.

stays relatively constant, and then decreases dramatically. The soaking time is the more significant variable for the improvement of porosity in activated carbon.  $H_3PO_4$  has two significant functions: it stimulates the pyrolytic decomposition of the original material and the development of the cross-linked structure. Though,  $H_3PO_4$  allows the increase of both micropores and mesopores of the prepared activated carbon [45]. On the other hand, with the increase of soaking time with phosphoric acid, the samples were exposed to more acid (as in Fig. 12, saturation time > 12 h), overfull phosphoric acid could break carbon bond structures, which lead to damaging the pores of ACP-20%. For that reason, decreasing surface area and removal efficiency is expectable [44,45].

### 3.3.7. Effect of initial solution pH

The pH of the aqueous solution plays a critical role in adsorption uptake [10,13,46]. The extent of electrostatic charges conveyed by the ionized TOC ions of soap solution and the functional groups on the ACP-20% surface are primarily controlled by pH of the medium [16]. The effect of solution pH on the removal efficiency and adsorption capacity of TOC from aqueous soap solution using pine cone and  $H_3PO_4$  treated pine cone powder is shown in Fig. 13.

Fig. 13 demonstrates the relationship between amounts of TOC adsorbed and initial solution pH. It is obvious that increasing the solution pH will decrease the removal efficiency. At value 4 of solution pH, more TOC is removed from the solution than with any other initial solution pH tested. This can be explained by the positive charge of the ACP-20% surface and by the electrostatic attraction between negative adsorbate and positive surface causing high removal percentage. The HCl-treated samples had higher TOC adsorption capacities than the untreated ones. As solution pH increases, the TOC capacities of the samples increase up to a solution pH of 7.0. After initial solution pH of 7.0, the adsorption capacities for TOC samples were found to decrease. This can be attributed to a pH > 7.0, repulsion between anionic TOC and negative surface, and also competitive adsorption between  $OH^-$  of solution and anion of

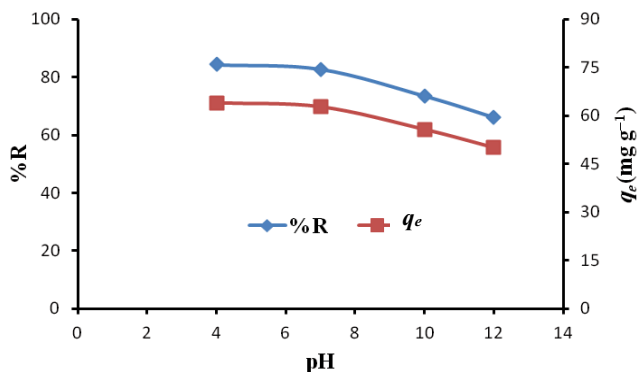


Fig. 13. Effects of solution pH on removal efficiency and adsorption capacity of ACP-20% for removal of TOC ( $758 \text{ mg L}^{-1}$ ) from aqueous solution, acid concentration 20 wt%, irradiation time 4 min, saturation time 24 h, biosorbent dosage 1 g.

TOC causing low removal efficiency [16]. These results are in good agreement with reported finding of Emami and Azizian [10]. Furthermore, and as per above results, in order to prepare ACP, it seems that, phosphoric acid of 40%, microwave power level of 700 W and radiation time of 2 min with pH of 2 are the optimum conditions.

### 3.4. TOC adsorption kinetics

A study of adsorption kinetics is significant as it provides information on the adsorption mechanism, which is critical for the practicality of the process, which is helpful for selecting optimum operating conditions for the full-scale batch process [10,32]. In our case, two different kinetic models, pseudo-first-order and pseudo-second-order kinetic models, at two different concentration levels, were applied in order to determine which of them shows the best fit with experimentally obtained data [10,13,47].

#### 3.4.1. Pseudo-first-order model

Pseudo-first-order rate equation, which is dependent on adsorption capacity, is one of the most kinetic equations [10,20,47–49]. To differentiate kinetic equations depended on adsorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order. In recent years, it has been generally used to explain the adsorption of pollutants from wastewater in different fields [50].

The integrated form of this model can be given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant and time  $t$ .

The initial adsorption rate,  $h$  ( $\text{mg g}^{-1} \text{ min}^{-1}$ ), at  $t = 0$  is defined from Eq. (5) [51]:

$$h = k_1 q_e^2 \quad (5)$$

where  $k_1$  and  $h$  values were determined from the slope and intercept of the plots of  $\log(q_e - q_t)$  against  $t$  (Fig. 14).

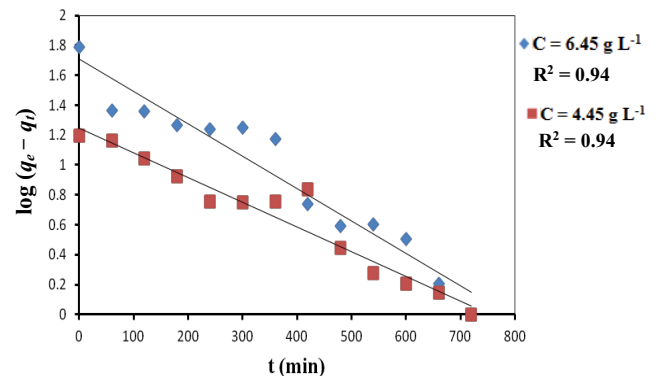


Fig. 14. Pseudo-first-order plot for TOC adsorbate on ACP at different Tide soap concentrations 4.45 and 6.45  $\text{g L}^{-1}$ .

The values of the parameters and correlation coefficient are also presented in Table 4. The correlation coefficient of examined data was found high ( $R^2 > 0.93$ ). It was observed that the equilibrium is reached within 7 h for TOC. This shows that the adsorption of TOC onto ACP-20% followed the pseudo-first-order kinetic model. The overall rate constants for adsorption were determined from slopes of the plots and listed in Tables 4 and 5. The rate constant was higher at higher concentrations.

3.4.2. Pseudo-second-order model

Qiu et al. [50] illustrated a kinetic process of the adsorption of divalent metal ions onto peat, where the chemical bonding was among divalent metal ions and polar functional groups on peat. Also, Qiu et al.'s [50] second-order rate equation has been called pseudo-second-order rate equation to distinguish kinetic equations based on adsorption capacity from concentration of solution. This equation has been effectively applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions [50]. The following equation is the integrated form of pseudo-second-order rate equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the pseudo-second-order rate constant [10,16,20,47–49]. The initial adsorption rate,  $h$  ( $\text{mg g}^{-1} \text{min}^{-1}$ ), at  $t = 0$ , is defined as follows [51]:

$$h = k_2 q_e^2 \tag{7}$$

By applying pseudo-first-order kinetic model, the value of adsorption rate constant  $k_1$  for the TOC adsorption onto ACP-20% was determined from the straight line plot of  $\log(q_e - q_t)$  against  $t$  (Fig. 15). These results indicate that increase in TOC concentration increased the adsorption rate constants.

The data were fitted with a weak correlation coefficient (Table 5), indicating that the rate of removal of TOC onto

ACPP-20% does not follow the pseudo-second-order equation. Value of the adsorption rate constant  $k_1$  for the TOC adsorption onto ACP-20% was derived from the straight line plot of  $t/q_t$  against  $t$  (Fig. 14). A correlation coefficient was added to fit the data (Table 5), showing that the removal rate of TOC onto ACP-20% does not conform to the pseudo-second-order equation. Therefore, Lagergren's model could be used for the prediction of the kinetics of adsorption of TOC on ACP-20%.

3.5. TOC adsorption isotherms

The relation between the amounts of adsorbate species and the equilibrium concentration is identified as adsorption isotherm. The equilibrium experimental data were analyzed by applying most used two models, including Langmuir and Freundlich isotherms [10]. These models were applied to investigate an interaction of adsorbate molecules and adsorbent surface [47].

3.5.1. Langmuir isotherm model

The Langmuir isotherm contains several hypotheses, which are surface homogeneity in character, and possesses identical and energetically equivalent adsorption sites and absence of interactions between adsorbed molecules on the surface. In addition, the formation of monolayer occurs on the surface of the adsorbent, indicating that only one TOC molecule could be adsorbed on one adsorption site and the

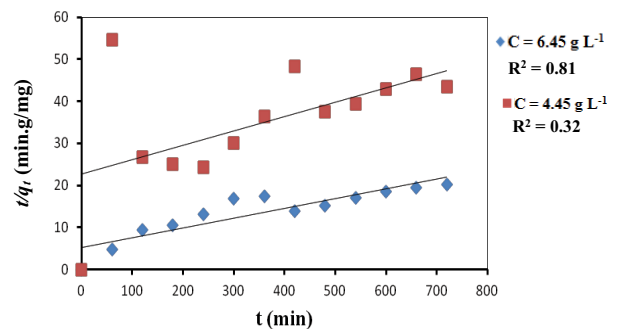


Fig. 15. Pseudo-second-order plot for TOC adsorbate on ACP-20% at different Tide soap concentrations 4.45 and 6.45  $\text{g L}^{-1}$ .

Table 4  
Pseudo-first-order model rate constants for ACP-20%

$R^2$	$h$	$k_1$	$q_e$ ( $\text{mg g}^{-1}$ )	Concentration of TOC ( $\text{mg L}^{-1}$ )	Concentration of Tide soap ( $\text{g L}^{-1}$ )
0.936	13.250	0.005	51.480	616	6.45
0.926	1.260	0.004	17.760	381	4.45

Table 5  
Pseudo-second-order model rate constants for ACP-20%

$R^2$	$H$	$k_2$	$q_e$ ( $\text{mg g}^{-1}$ )	Concentration of TOC ( $\text{mg L}^{-1}$ )	Concentration of Tide soap ( $\text{g L}^{-1}$ )
0.809	0.0045	$1.02 \times 10^{-4}$	43.290	616	6.45
0.320	0.045	$5.13 \times 10^{-5}$	29.330	381	4.45



intermolecular forces decrease with the distance [10,47]. The Langmuir equation can be written as:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{8}$$

where  $q_{\max}$  (mg g<sup>-1</sup>) and  $K_L$  (L mg<sup>-1</sup>) are known as Langmuir constants and refer to maximum sorption capacity and affinity of sorption, respectively [10,16,20,47–49].

A linear Langmuir adsorption isotherm is shown in Fig. 16. The values of  $q_{\max}$  and  $K_L$  of linear expression of Langmuir adsorption isotherm were calculated from the slopes and intercept of the linear plot of  $C_e/q_e$  vs.  $C_e$  in Fig. 16 and Table 6, according to Eq. (9).

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left( \frac{1}{k_L q_{\max}} \right) \left( \frac{1}{C_e} \right) \tag{9}$$

The linearity of the isotherm through the entire concentration range studies, with a good linear correlation coefficient ( $R^2 = 0.9113$ ) (as per Table 6), shows that Langmuir equation is the best fit for the experimental data compared with the other isotherm equation. This confirms the monolayer coverage of TOC onto ACP-20% particles ( $q_{\max} = 8.56 \text{ mg g}^{-1}$ ) as well as the homogeneous distribution of active sites on the adsorbent, given that the Langmuir equation assumes homogeneity of the surface [47].

The main features of the Langmuir isotherm can be expressed in expressions of a dimensionless constant called separation factor ( $R_L$ , also called equilibrium parameter) which is determined by the following Eq. (10) [46]:

$$R_L = \frac{1}{1 + k_L C_0} \tag{10}$$

The value of  $R_L$  indicates the shape of the isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

The impact of the isotherm shape on whether adsorption is favorable or unfavorable has been considered. By a Langmuir type adsorption process, the isotherm shape can

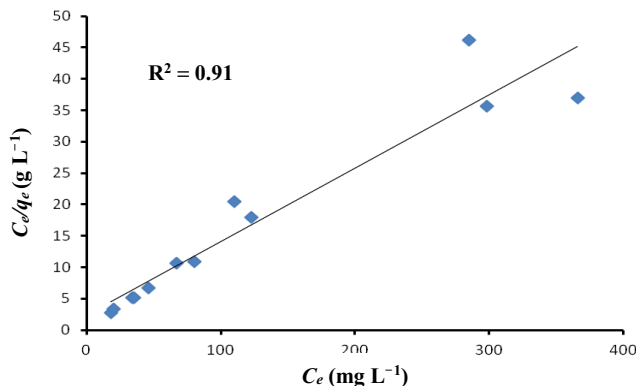


Fig. 16. Linear Langmuir adsorption isotherm.

be classified by a measurement less a constant separation factor ( $R_L$ ), given via Eq. (10). The calculated  $R_L$  values as different initial TOC concentrations are shown in Fig. 17. It was observed that the value of  $R_L$  in the range 0-1 confirms the favorable uptake of the TOC process. Furthermore, lower  $R_L$  values at higher initial TOC concentrations showed that adsorption was more appropriate at higher concentration. The degree of favorability is mostly related to the irreversibility of the system, giving a qualitative estimate of the ACP-20%–TOC interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which characterizes a completely reversible case) [47].

### 3.5.2. Freundlich isotherm model

The Freundlich isotherm is an experimental equation, utilized for heterogeneous surfaces [10,47]. The Freundlich isotherm is given as follows:

$$q_e = K_F C_e^{1/n} \tag{11}$$

where  $K_F$  (mg<sup>1-(1/n)</sup> L<sup>1/n</sup>/g) is Freundlich constant and  $n$  indicates sorption heterogeneity [10,13,16,19,32]. Eq. (11) can be rearranged to obtain a linear form by taking logarithms Eq. (12):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{12}$$

The slope and the intercept correspond to  $(1/n)$  and  $k_f$  respectively. It was revealed that the plot of  $\ln q_e$  and  $\ln C_e$  yields a straight line (Fig. 18). The results are indicated in Table 6. The appropriate adsorption of this model can be described such that if a value for  $n$  is above unity, adsorption is appropriate and a physical process [47]. In the present

Table 6  
Langmuir and Freundlich adsorption isotherm constants

Langmuir			Freundlich		
$q_{\max}$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R^2$	$n$	$k_f$	$R^2$
8.560	0.049	0.91	4.190	2.180	0.35

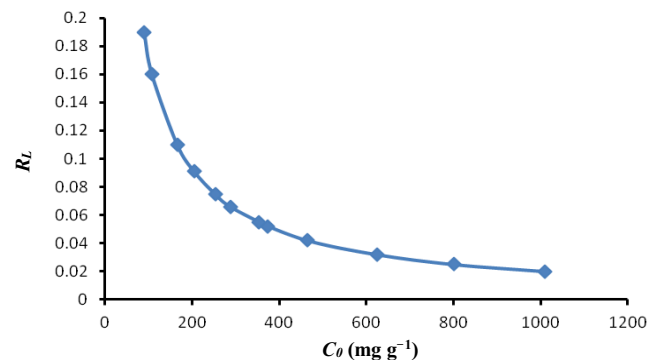


Fig. 17. Plot of separation factor vs. initial TOC concentration.

study the value of  $n$  ( $n = 4.190$ ) is greater than 1, indicating that the adsorption process is appropriate. However the value of correlation coefficient ( $R^2 = 0.3498$ ) is much lower than the Langmuir isotherm value.

### 3.6. Thermodynamic study

The effect of temperature on the thermodynamic TOC adsorption on the ACP-20% was investigated from 12°C to 50°C (Fig. 19). The thermodynamic parameters including change in the Gibbs free energy,  $\Delta G^\circ$  (kJ mol<sup>-1</sup>), enthalpy,  $\Delta H^\circ$  (kJ mol<sup>-1</sup>) and entropy,  $\Delta S^\circ$  (J mol<sup>-1</sup> K<sup>-1</sup>), were determined by means of the following equations and represented in Table 7:

$$K_c = \frac{q_e}{C_e} \quad (13)$$

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

where  $R$  = gas constant,  $K_c$  = equilibrium constant, represents the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate (TOC) within the solution [9,46,51].  $K_c$  is the ratio of the final or equilibrium concentration of the TOC ( $q_e$ ) attached to adsorbent compared with the Van't Hoff equation as equilibrium TOC concentration in solution ( $C_e$ ), Eq. (13). It was given the plot of  $\ln K_c$  vs.  $1/T$  to Eq. (15) and Fig. 18.  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from this plot (Van't Hoff plots) [9,47,52].

Thermodynamic parameters obtained are given in Table 7.  $K_c$  indicates the capability of the ACP-20% to retain a solute and also the extent of its movement in a solution phase [21]. As shown in Table 7,  $\Delta G^\circ$  is slightly increasing with the increasing temperature from 12°C to 50°C. The negative values of  $\Delta G^\circ$  at different temperatures indicate the feasibility of the process and the spontaneous nature of

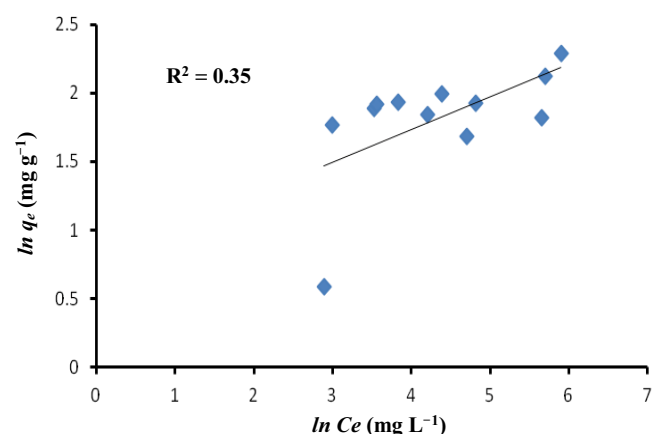


Fig. 18. Linear Freundlich adsorption isotherm.

the adsorption [23,52]. Generally, the change in adsorption enthalpy for physisorption is in the range of -20 to 40 kJ mol<sup>-1</sup>, but chemisorption is between -400 and -80 kJ mol<sup>-1</sup> [47]. The negative  $\Delta H^\circ$  (-2.500 kJ mol<sup>-1</sup>) reveals the adsorption is exothermic and physical in nature [9,47]. Furthermore, slightly positive  $\Delta S^\circ$  of TOC adsorption process indicates an irregular increase of the randomness at the ACP-20% solution interface during adsorption.

### 3.7. Comparison with other various solid bio-adsorbents

Different kinds of natural and modified adsorbents were used in TOC removal from water. TOC adsorption on a variety of adsorbents was widely referred to in the literature. Table 8 shows a comparison on removal efficiency of TOC with various adsorbents of natural, modified, and synthetic adsorbents. The removal efficiency of TOC depends on kinds of TOC and adsorption conditions.

From Table 8, the highest removal efficiency of granular activated carbon (0.3–2.38 mm diameter) is due to the highest specific surface area (1,000 mg mg<sup>-1</sup>) [53]. The adsorption capacity of ACP-20% is comparable with other adsorbents [35,53]. The maximum removal efficiency of TOC (%R) achieved with ACP-20% is 87.71%, which is suitable for ACP-20% to be an adsorbent, with the benefit of easy handling and cost effectiveness. NPC modified with H<sub>3</sub>PO<sub>4</sub>/MW proves as an attractive alternative for TOC adsorption.

## 4. Conclusions

In conclusion, the present investigation showed that “cone of pine”, which is the product from widely planted

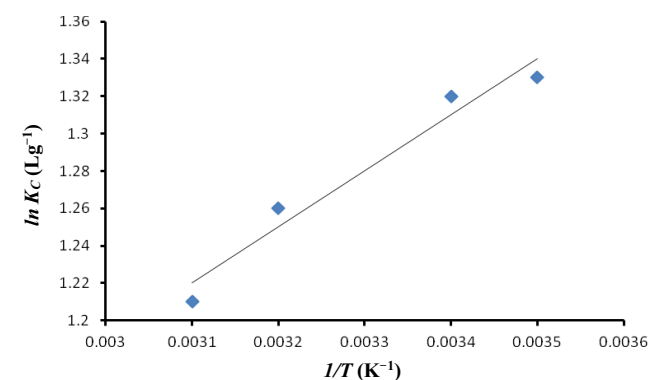


Fig. 19. A plot of  $\ln K_c$  vs.  $1/T$  for TOC Adsorption onto ACP-20% for 758 mg/L initial concentration (Tide soap 6.45 g/L) at constant adsorbents dose: 1 g/100 mL.

Table 7

Value of the thermodynamic of TOC adsorption by ACP-20% at various temperatures and at different composition of mixture

$-\Delta G^\circ$ (kJ mol <sup>-1</sup> )				$\Delta H^\circ$	$\Delta S^\circ$
50°C	37°C	22°C	12°C	(kJ mol <sup>-1</sup> )	(J mol <sup>-1</sup> K <sup>-1</sup> )
3.280	3.240	3.210	3.190	-2.500	2.410

Table 8  
Comparison of removal efficiency of TOC with various adsorbents

Adsorbent	Removal efficiency (%R)	References
ACPP-20%	87.71	This study
D-glucose	44%–58%	[35]
1.2 mm dia.	21	[53]
Calgon F820, 1 mm dia.	50	[53]
Granular activated carbon 0.3 mm	81–87.5	[53]
Granular activated carbon 0.3–2.38 mm diameter	99	[54]
Powdered activated carbon	Above 60	[53]

tree of the local area of Mount Royal in Montreal, Quebec, can be effectively used as a raw material for the preparation of activated carbon by chemical activation. The presented results demonstrate that microwave heating is an effective, facilitate and cost-effective method that for the production of activated carbon having high adsorption capacity and removal efficiency. The most effective activated carbon was obtained with: phosphoric acid concentration of 20%, initial solution pH of 4, soaking time of 12 h, low temperature of 12°C and radiation time of 4 min. The Freundlich theoretical describes well the results obtained from this study; however the Langmuir equation represented the best fit of experimental data. As indicated by the kinetic data, the adsorption process follows the first-order equation. Thermodynamic studies indicated that adsorption of TOC on ACPP-20% was stable over an extensive range of temperature; it was also exothermic and took place spontaneously in nature. The prepared active carbon is an effective and low-cost adsorbent for removal of TOC from laundry aqueous media. Reuse of spent ACPP and recovery of adsorbed TOC may also be of further scope of research.

### Acknowledgments

The authors would like to thank the Experimental Station for Environmental Pilot Processes, Ecole de technology superior and the Ministry of Higher Education Libya for scholarship to Said Mussa Hafyana.

### References

- [1] K. Press-Kristensen, A. Ledin, J.E. Schmidt, M. Henze, Identifying model pollutants to investigate biodegradation of hazardous XOCs in WWTPs, *Sci. Total. Environ.*, 373 (2007) 122–130.
- [2] E. Eriksson, K.P.S. Auffarth, A.M. Eilersen, M. Henze, A. Ledin, Household chemicals and personal care products as sources for xenobiotic organic compounds in grey wastewater, *Water S.A.*, 29 (2003) 135–146.
- [3] D. Christova-Boal, R.E. Eden, S. McFarlane, An investigation into greywater reuse for urban residential properties, *Desalination*, 106 (1996) 391–397.
- [4] J.K. Braga, M.B.A. Varesche, Commercial Laundry Water Characterisation, *Am. J. Anal. Chem.*, 5 (2014) 8–16.
- [5] E. Eriksson, Potential and Problems Related to Reuse of Water in Households, Kgs. Lyng by: Environment & Resources DTU Technical University of Denmark, 2002, p. 41.
- [6] L. Allen, J. Christian-Smith, M. Palaniappan, Overview of greywater reuse: the potential of greywater systems to aid sustainable water management, Pacific Institute, 2010, p. 654.
- [7] R.K. Misra, A. Sivongxay, Reuse of laundry greywater as affected by its interaction with saturated soil, *J. Hydrol.*, 366 (2009) 55–61.
- [8] C.D. Grant, The Nature and Properties of Soils, 13th Edition: N.C. Brady, R.R. Weil, Eds., Prentice Hall, Upper Saddle River, NJ, Vol. 95, 2003, p. 960.
- [9] N. Babakhouya, S. Boughrara, F. Abad, Kinetics and thermodynamics of Cd(II) ions sorption on mixed sorbents prepared from olive stone and date pit from aqueous solution, *Am. J. Enol. Sci.*, 6 (2010) 470–476.
- [10] Z. Emami, S. Azizian, Preparation of activated carbon from date sphate using microwave irradiation and investigation of its capability for removal of dye pollutant from aqueous media, *J. Anal. Appl. Pyrolysis*, 108 (2014) 176–184.
- [11] E.L. Terechova, G. Zhang, J. Chen, N.A. Sosnina, F. Yang, Combined chemical coagulation–flocculation/ultraviolet photolysis treatment for anionic surfactants in laundry wastewater, *J. Environ. Chem. Eng.*, 2 (2014) 2111–2119.
- [12] N. Das, R. Vimala, P. Karthika, Biosorption of heavy metals—an overview, *Indian J. Biol.*, 7 (2008) 159–169.
- [13] M. Momčilović, M. Purenović, A. Bojić, A. Zarubica, M. Randelović, Removal of lead (II) ions from aqueous solutions by adsorption onto pine cone activated carbon, *Desalination*, 276 (2011) 53–59.
- [14] W. Cheng, S. Dastgheib, T. Karanfil, Adsorption of dissolved natural organic matter by modified activated carbons, *Water Res.*, 39 (2005) 2281–2290.
- [15] S. Velten, D.R.U. Knappe, J. Traber, H.P. Kaiser, U. von Gunten, M. Boller, S. Meylan, Characterization of natural organic matter adsorption in granular activated carbon adsorbents, *Water Res.*, 45 (2011) 3951–3959.
- [16] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Removal of copper (II) from aqueous solution by pine and base modified pine cone powder as biosorbent, *J. Hazard. Mater.*, 168 (2009) 909–917.
- [17] T. Matsuo, T. Nishi, Activated carbon filter treatment of laundry waste water in nuclear power plants and filter recovery by heating in vacuum, *Carbon*, 38 (2000) 709–714.
- [18] K.J. Kim, H.G. Ahn, The effect of pore structure of zeolite on the adsorption of VOCs and their desorption properties by microwave heating, *Microporous Mesoporous Mater.*, 152 (2012) 78–83.
- [19] S.M. Michaelson, Biological Effects and Health Hazards of RF and MW Energy: Fundamentals and Overall Phenomenology, NATO Advanced Study Institutes Series, Springer, Boston, 1983.
- [20] O. Ilomuanya Margaret, Billa Nashiru, D. Ifudu Ndu, I. Igwilo Cecilia, Effect of pore size and morphology of activated charcoal prepared from midribs of *Elaeis guineensis* on adsorption of poisons using metronidazole and *Escherichia coli* O157:H7 as a case study, *J. Microsc. Ultrastruct.*, 5 (2017) 32–38.
- [21] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design, *Water Res.*, 46 (2012) 1933–1946.
- [22] A. Dehdashti, A. Khavanin, A. Rezaee, H. Assilian, M. Kashani, Application of microwave irradiation for the treatment of

- adsorbed volatile organic compounds on granular activated carbon, Iran. J. Environ. Health Sci. Eng., 8 (2011) 85–94.
- [23] E.A. Moawed, M.F. El-Shahat, Equilibrium, kinetic and thermodynamic studies of the removal of triphenyl methane dyes from wastewater using iodopolyurethane powder, J. Taibah Univ. Sci., 10 (2016) 46–55.
- [24] H. Rungping, Z. Jingjing, H. Pan, W. Yuanfeng, Z. Zhenhui, T. Mingsheng, Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite, Chem. Eng. J., 145 (2009) 496–504.
- [25] M.E. Argun, S. Dursun, K. Gur, C. Ozdemir, M. Karatas, S. Dogan, Nickel adsorption on the modified pine tree materials, Environ. Technol., 26 (2005) 479–488.
- [26] D. Nilanjana, R. Vimala, P. Karthika, Biosorption of heavy metals—an overview, Indian J. Biotech., 7 (2008) 159–169.
- [27] D. Florescu, I. Andreea Maria, C. Diana, E. Horj, I. Roxana, M. Culea, Validation procedure for assessing the total organic carbon in water samples, Rom. J. Phys., 58 (2013) 211–219.
- [28] T. Santhi, A.L. Prasad, S. Manonmani, A comparative study of microwave and chemically treated *Acacia nilotica* leaf as an eco friendly adsorbent for the removal of rhodamine B dye from aqueous solution, Arabian J. Chem., 7 (2014) 494–503.
- [29] S. Cheng, J. Wu, H. Xia, J. Peng, S. Wang, L. Zhang, Microwave-assisted regeneration of spent activated carbon from paracetamol wastewater plant using response surface methodology, Des. Water Treat., 57 (2016) 18981–18991.
- [30] N. Rambabu, S. Panthapulakkal, M. Sain, A.K. Dalai, Production of nanocellulose fibers from pinecone biomass: evaluation and optimization of chemical and mechanical treatment conditions on mechanical properties of nanocellulose films, Ind. Crop. Prod., 83 (2016) 746–754.
- [31] N. Mabaso, B. Naidoo, A. Ofomaja, H. Chiririwa, Synthesis, structural and morphological studies of pine cone powder by Fenton oxidation and grafting with acrylic acid using Ammonium ceric nitrate as initiator, Nat. Prod. Ind. J., 14 (2018) 116.
- [32] T. Zhang, J. Mao, X. Liu, M. Xuan, K. Bi, X.L. Zhang, J. Hu, J. Fan, S. Chen, G. Shao, Pinecone biomass-derived hard carbon anodes for high-performance sodium-ion batteries, RSC Adv., 7 (2017) 41504–41511.
- [33] Y. Zhang, R. Zheng, J. Zhao, F. Ma, Y. Zhang, Q. Meng, Characterization of H<sub>3</sub>PO<sub>4</sub>-treated rice husk adsorbent and adsorption of copper(II) from aqueous solution, BioMed Res. Int., 2014 (2014) 496878.
- [34] S. Salimian, M. Kamali moghaddam, S. Safi, S.M. Mortazavi, Properties of wool dyed with pinecone powder as a by-product colorant, Indian J. Fibre Text., 41 (2016) 173–179.
- [35] P.T. Huong, B.K. Lee, J. Kim, C.H. Lee, M.N. Chong, Acid activation pine cone waste at differences temperature and selective removal of Pb<sup>2+</sup> ions in water. Process Saf. Environ., 100 (2016) 80–90.
- [36] W.T. Mook, M.H. Chakrabarti, M.K. Aroua, G.M.A. Khan, B.S. Ali, M.S. Islam, M.A. Abu Hassan, Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: a review, Desalination, 285 (2012) 1–13.
- [37] K. Karthikeyan, S. Amaresh, S.N. Lee, X. Sun, V. Aravindan, Y.-G. Lee, Y.S. Lee, Construction of high-energy-density supercapacitors from pine-cone-derived high-surface-area carbons, ChemSusChem, 7 (2014) 1435–1442.
- [38] Ar A. Dehdashti, A. Khavanin, A. Rezaee, H. Asilian, Regeneration of granular activated carbon saturated with gaseous toluene by microwave irradiation, Turkish J. Eng. Environ. Sci., 34 (2010) 49–58.
- [39] Z. Milan Momčilović, E. Onjia Antonije, M. Milovan Purenović, R. Aleksandra Zarubica, S. Marjan Randelović, Removal of a cationic dye from water by activated pinecones, J. Serb. Chem. Soc., 77 (2012) 761–774.
- [40] K. Kaliyappan, S. Amaresh, S.N. Lee, X. Sun, V. Aravindan, Y.G. Lee, Y.S. Lee, Constructing high energy density supercapacitors from pinecone derived high surface area carbons, ChemSusChem, 7 (2014) 1435–1442.
- [41] M. Kruk, M. Jaroniec, Gas adsorption characterization of ordered organic–inorganic nanocomposite materials, Chem. Mater., 13 (2001) 3169–3183.
- [42] G. Gong, D. Liu, Y. Huang, Microwave-assisted organic acid pretreatment for enzymatic hydrolysis of rice straw, Biosyst. Eng., 107 (2010) 67–73.
- [43] L. Wu, X. Zhang, D. Liu, H. Peng, T. Long, Activated carbons derived from livestock sewage sludge and their absorption ability for the livestock sewage, IERI Procedia, 9 (2014) 33–42.
- [44] K. Kumar, R. Kothari, R.K. Saxena, K.N. Kaushik, J.N. Bohra, Effect of soaking time at maximum heat treatment temperature on the pore structure of chars derived from viscose rayon cloth, J. Chem. Tech., 5 (1998) 131–134.
- [45] A. Kumar, H.M. Jena, Preparation and characterization of high surface area activated carbon from Fox nut (*Euryale ferox*) shell by chemical activation with H<sub>3</sub>PO<sub>4</sub>, Res. Phys., 6 (2016) 651–658.
- [46] S. Debnath, N. Ballav, A. Maity, K. Pillay, Competitive adsorption of ternary dye mixture using pine cone powder modified with  $\beta$ -cyclodextrin, J. Mol. Liq., 225 (2017) 679–688.
- [47] B. Meroufel, O. Benali, M. Benyahia, Y. Benmoussa and M.A. Zenasni, Adsorptive removal of anionic dye from aqueous solutions by Algerian kaolin: characteristics, isotherm, kinetic and thermodynamic studies, J. Mater. Environ. Sci., 4 (2013) 482–491.
- [48] K. Vasanth Kumar, Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon, J. Hazard. Mater. B, 137 (2006) 1538–1544.
- [49] Y. Zhan, Z. Zhu, J. Lin, Y. Qiu, J. Zhao, Removal of humic acid from aqueous solution by cetylpyridinium bromide modified zeolite, J. Environ. Sci., 22 (2010) 1327–1334.
- [50] H. Qiu, L. Lv, B. Pan, Q. Zhang, W. Zhang, Q. Zhang, Critical review in adsorption kinetic models, J. Zhejiang Univ. Sci. A, 10 (2009) 716–724.
- [51] B.H. Hameeda, M.I. El-Khaiary, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: equilibrium isotherms and kinetic studies, J. Hazard. Mater., 154 (2008) 237–244.
- [51] S. Abdel Wanees, M. Monem, A. Ahmed, M.S. Adam, M.A. Mohamed, Adsorption Studies on the Removal of Hexavalent Chromium-Contaminated Wastewater Using Activated Carbon and Bentonite, Asian J. Chem., 25 (2013) 8245–8252.
- [52] J.W. Hatt, E. Germain, S.J. Judd, Granular activated carbon for removal of organic matter and turbidity from secondary wastewater, Water Sci. Technol., 846 (2013) 846–853.
- [53] T. Mohammed, S. Vigneswaran, J. Kandasamy, Biofiltration as pre-treatment to water harvesting and recycling, Water Sci. Technol., 63 (2011) 2097–2105.