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Solid olive waste in environmental cleanup: Enhanced nitrite ion removal by $ZnCl_2$-activated carbon

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ABSTRACT

This communication describes how olive solid wastes can be used to prepare activated carbon (AC), with soundly high surface areas, suitable to remove nitrite ions from water. Solid olive wastes, so called *Jeft*, separated as unwanted bi-products from olive oil mills, have been converted into charcoal. The charcoal was then physically and/or chemically activated using different compounds namely conc. H_3PO_4 or $ZnCl_2$. Charcoal carbonization was performed under inert atmosphere to avoid loss of heated carbon by oxidation with air. Surface area measurements and SEM micrographs showed that activation using $ZnCl_2$ yields AC with highest surface area and more porous surfaces. The $ZnCl_2$-activated carbon was then used to remove nitrite ions from water by adsorption. Effects of different parameters on value of surface area and adsorption capacity of the AC were investigated. Commercial AC materials were used as reference for comparison. The AC showed higher adsorption capacity toward nitrite than other reported adsorbents. The results suggest that using 5 g of the $ZnCl_2$-activated carbon per liter of heavily nitrite-contaminated water (50 ppm) may bring the contaminant concentration down to the WHO accepted concentration limits within 60 min. This work highlights the future feasibility of using olive waste as feed stocks to produce useful renewable materials while keeping in mind the wisdom "*make wastes work in environmental protection*".

1. Introduction

In a preceding communication (El-Hamouz et al., 2007), olive solid wastes were used to produce charcoal materials useful for reversible adsorption of chromium ions from water. In this report, attention has been paid to find best methods to activate the olive solid waste-based charcoal materials. The prepared activated carbon (AC) materials have then been characterized by their surface morphology and relative surface areas. Adsorption efficiency of the resulting materials has been tested using a hazardous water contaminant, nitrite ion, as a model adsorbate.

The idea of using carbon produced from agricultural wastes in water purification is not new. Man wisely used such methods long time ago (Al-Swaidan and Ahmad, 2011; Cheremisinoff and Ellerbusch, 1978; Karthikeyan et al., 2008; Smâiések and éCernây, 1970). Currently, carbons produced from different agricultural sources are being activated in different ways so as to maximize their surface areas and increase their adsorption capacity (Angin, 2013; Jimenez-Cordero et al., 2014; Libra et al., 2011; Martínez de Yuso et al., 2014; Velo-Gala et al., 2013). Two methods are commonly used, namely physical activation and chemical activation. In chemical activation, which is considered more economic due to lower needed processing temperatures, the charcoal material is typically impregnated and pyrolyzed (Caturla et al., 1991; Yavuz et al., 2010). The remaining activating agent is then removed away. Many types of substances have been investigated as activating agents, such as potassium hydroxide (Bagheri and Abedi, 2009; Tseng, 2007), sodium hydroxide (Budinova et al., 2006; Sun et al., 2012), sulfuric acid (Bagheri and Abedi, 2009), hydrochloric acid (Yavuz et al., 2010), phosphoric acid (Lafi, 2001; Martinez et al., 2006; Puziy et al., 2003, 2002; Williams and Reed, 2006), calcium chloride (El-Hamouz et al., 2007; Yavuz et al., 2010), aluminum chloride, potassium chloride (Baccar et al., 2009), zinc chloride (Angin, 2013; Caturla et al., 1991; Kopac and Toprak, 2007; Petrov et al., 2008; Uğurlu et al., 2008, 2007), ammonium chloride (Moussavi et al., 2012; Rosas et al., 2009), potassium carbonate (Foo and Hameed, 2012; Liou, 2010; Mestre et al., 2011; Olivares-Marín

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et al., 2006) and sodium carbonate (Liou, 2010).

This work aims at preparing AC from olive solid wastes to be used in removal of hazardous substances, such as nitrite ions, from water. Two reported activating agents, namely zinc chloride and phosphoric acid, will be examined here. Neither of such compounds has any serious threat to health or environment as reported in their Material Safety Data Sheets (MSDS). The carbonization step will be performed under inert atmosphere to avoid oxidation (burning) of heated charcoal during carbonization. The AC materials resulting from using the two activating agents will be characterized for comparison purposes. Bench marking with documented commercial activated carbon (CAC) material will be investigated here, in addition to comparison with other reported adsorbents. The material of choice will then be investigated as an adsorbent for nitrite ions from water.

Literature described removal of nitrite ions from water by adsorption, using carbon cloth, activated carbon and other materials (Afkhami, 2003; Afkhami et al., 2007; Neşe and Ennil, 2008; Otten et al., 2012). To our knowledge, AC materials obtained from olive solid wastes have not been widely described for nitrite ion removal from water. The nitrite ions have been chosen as model contaminants due to their hazardous nature as defined by World Health Organization (WHO) (Organization, 2004). The toxicity of nitrite and nitrate ions, together with their occurrence in environment, is well described elsewhere (Ayyasamy et al., 2009; Melchert et al., 2007; Mikuška and Večeřa, 2003; Mishra and Patel, 2009; Mizuta et al., 2004; Okafor and Ogbonna, 2003; Öztürk and Bektaş, 2004; Tu et al., 2012), and needs no further elaboration. Removal of nitrite ions from water should be of prime importance to environment and health. Comparison of $ZnCl_2$-activated carbon with other reference adsorbents, in terms of adsorption capacity, will be highlighted in this work.

2. Experimental

2.1. Chemicals

All used chemicals were of analytical grade and were used without further purification. Phosphoric acid (85%), methanol, toluene, acetic acid, diphenyl amine and sodium hydroxide were all purchased from Frutarom. Potassium hydrogen phthalate (KHP) and zinc chloride were purchased from Alfa Aeser, and sodium nitrite from Avokado. Commercial granular activated carbon (CAC), Aktivkohle (Hydraffin CC8X30), from Donau Carbon, with surface area (1000 m^2/g), and particle size (0.5–2.5 mm) (Kaya et al., 2008) was used, without treatment, as benchmark adsorbent.

Wet olive waste (*Jeft*) byproduct collected from oil mills in Nablus area, Palestine, was used as raw material for the production of activated carbon. The *Jeft* samples were collected during the olive cultivation season (October–December) and stored in a refrigerator for further use.

2.2. Preparation of AC materials

A stepwise process was followed to prepare AC materials, as follows:

2.2.1. Pre-treatment of Jeft

Lignocellulosic materials, hemicellulose, cellulose and lignin are the main components of olive stone, in addition to fats, proteins, water-soluble carbohydrates and phenolic compounds (Alburquerque et al., 2004; Rodríguez et al., 2008). *Jeft* involves crushed hard olive stones, soft pulp, moisture and oil remains. The soft pulp was mainly removed away by immersing the raw material in tap water. The soft pulp particulates floated onto the water surface allowing easy separation by decantation. The desired olive stones were separated and dried in an oven at 110 °C. The resulting particles were then sieved, with the range (1.18–2.36 mm) taken for further processing. Any oil remaining in the olive stones was removed by extraction using a Soxhlet apparatus, as described earlier (El-Hamouz et al., 2007) with modification. Solvent toluene (300 mL) was refluxed over olive stone (100.00 g) in a 1.0 L Soxhlet apparatus for 20 min. The same toluene system (with oil inside) was repeatedly used 5 times, by replacing the solid stone batch with a fresh one every time. The oil was collected from the solution by toluene evaporation. In each distillation, the evaporated toluene was recovered in a cooled container, with percentage loss no more than 25%. The measured oil ratio inside the dried olive stones was only 1%. Parallel extraction experiments conducted on the raw wet *Jeft* showed that up to 7% of mass was oil, which confirms earlier findings (El-Hamouz et al., 2007). The resulting olive solid materials (termed as OS) were dried and stored to prepare activated carbons.

2.2.2. Carbonization procedure

A heavy duty tubular regulated furnace (Lindberg 9001) was used for carbonization. The pre-dried solid sample was inserted in the middle of the furnace using a 4 cm in diameter and 75 cm long cylindrical stainless steel tube. The furnace was heated to the desired carbonization temperature at a ramp (30 °C/min). The sample was kept at the desired temperature 450 °C for 2 h, under inert atmosphere (N_2 gas 99.9%) at a flow rate of about 0.5 L min^{-1}. The resulting carbon was cooled to room temperature under nitrogen flow. The resulting product yield was recorded.

2.2.3. Chemical activation

Different methods for carbon activation were followed, as described below, for comparison purposes. Samples (50.00 g) from same batch of pre-dried solid OS were used.

2.2.3.1. Activation with no agents. For comparison purposes, pre-dried olive stones were carbonized at 450 °C for 2 h without activating agents. After cooling, the sample was washed with deionized water, to remove dust, then dried in an oven at 110 °C and finally stored in a desiccator for further use. The resulting solid was termed (OSC).

2.2.3.2. Chemical activation with phosphoric acid. Phosphoric acid solution (100 mL, 50% w/w) was used in chemical activation of pre-dried OS. Literature suggests that such a concentration yields highest surface area for carbon activated by H_3PO_4 (Yavuz et al., 2010). The acid solution was mixed with the pre-dried olive stone sample, and the mixture was thoroughly stirred at 85 °C for 4 h. The solution was then filtered to separate the residual acid. The solid was then washed with deionized water, dried in an oven at (110 °C) and carbonized at 450 °C under nitrogen atmosphere as described above. The product was washed with hot deionized water and then with cold deionized water until the filtrate reached the pH range 4.5–5. The product was then dried in an oven at 110 °C and stored in a desiccator for further use. The resulting AC was termed H_3PO_4/450-AC.

2.2.3.3. Chemical activation with zinc chloride. Dried olive stone samples were mixed by stirring with zinc chloride solution (250 mL, 20% w/w) at room temperature for 24 h. This concentration gave highest surface area as described earlier (Uğurlu et al., 2008). Impregnation was then carried out at 70 °C in a water bath until excess water was evaporated. The samples were filtered and dried at 110 °C in an oven, without washing, before carbonization at 450 °C under inert atmosphere. The carbonized products were washed with 0.50 M hydrochloric acid solution, hot deionized

water and cold deionized water sequentially, to remove residual organic and mineral matters and to bring the pH within the range 4.5–5. The final product was dried in an oven at 110 °C and stored in a desiccator for further use. The resulting AC solid was termed $ZnCl_2$/450-AC. The general activation procedure discussed above is schematically outlined in Scheme 1 below. Table 1 summarizes preparation procedures for all AC samples described above.

2.3. AC characterization

The resulting AC solids were characterized by SEM and relative surface area (SA) measurement.

2.3.1. SEM micrographs

SEM micrographs were measured for different solid surfaces using a field emission scanning electron microscope (FE-SEM. JEOL JSM-6700F) with an energy dispersive X-ray spectrometer (EDS), at ICMCB, University of Bordeaux, France; and in Dansuk Industrial Co., LTD., Jeongwang-Dong, Shiheung-Si, Kyonggi-Do, South Korea.

2.3.2. Surface area measurement

Values of the relative surface area for different AC solids were measured by acetic acid adsorption, assuming a mono-layer coverage using Langmuir isotherms, as described earlier (Glasstone and Lewis, 1960). The BET method (using N_2 gas as adsorbate) was used to confirm the measured values. The relative surface area per gram of adsorbent was calculated assuming the cross sectional area per one acetic acid molecule is $2.1\,10^{-19}$ m^2 per molecule (Pashley and Karaman, 2005), and per one liquid N_2 molecule is $1.6\,10^{-19}$ m^2 (Arnett and Cassidy, 1988).

2.3.3. FT-Infra-red spectra

The FT-IR spectra were measured for solid activated carbon samples on a Thermo Fisher-ASB1200315-Nicolet 5 FT-IR Spectrometer. Measurements were made using single granules of the activated carbon material.

2.3.4. Thermal gravimetric analysis

TGA measurement for activated carbon samples were performed manually using a pre-calibrated muffle furnace and a Mettler balance. Activated carbon samples (1.000 g each) were placed in a pre-fired porcelain crucible. The mass was measured vs. temperature increase. Temperature was started at room temperature and was increased to 900 °C in the course of 120 min (ramp rate 2.3°/min).

Table 1
Summary of chemically AC materials prepared from pre-dried solid. All preparations were made using solution to solid mass ration 1:1.

Sample code	Activating agent	Carbonization temperature (°C)	Yield (%)[a]
OS	None	Non-carbonized	100%
OSC	None	450	34.90
H_3PO_4/450-AC	H_3PO_4 50% (by mass)	450	54.00
$ZnCl_2$/450-AC	$ZnCl_2$ 20% (by mass)	450	47.40

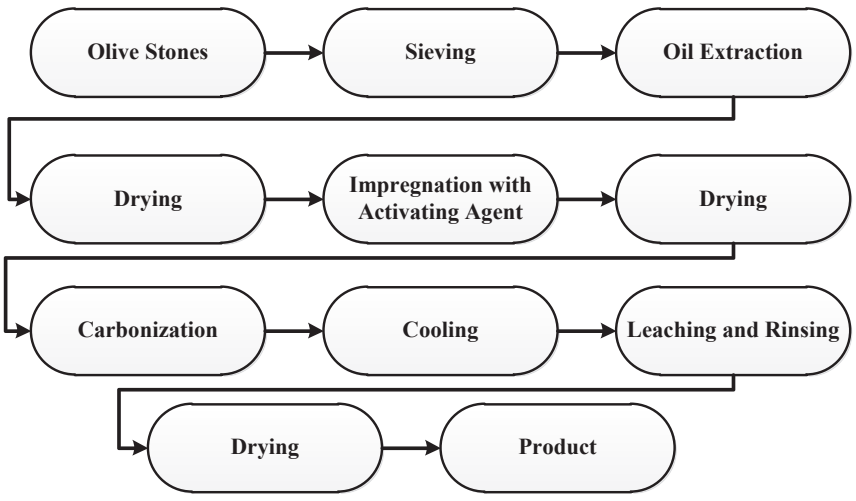
[a] Yield calculated with reference to original OS.

2.4. Adsorption experiments

Nitrite ion adsorption onto activated carbon surfaces was studied using batch systems. Additional experiments were performed on packed column flow systems as well. In batch system, experiments were conducted in a set of 100 mL pre-cleaned capped conical flasks, dipped inside a thermo-stated bath with continuous shaking (120 rpm). Nitrite solutions of known concentrations were added to AC samples of known amounts, after which the solution pH values were adjusted as desired by adding $NaOH_{(aq)}$ or $H_2SO_{4(aq)}$ solutions drop-wise. The column flow experiments were conducted by placing 1.0 g samples of activated carbon inside column with 0.5 cm in diameter. The AC column height was 3.0 cm. The nitrite solution was allowed to flow freely from a burette, through the AC column, and the flow rate was controlled to be 1.5 mL/min. Adsorption behaviors of AC prepared here were benchmarked with CAC described above.

2.5. Measurement of nitrite ion concentrations

Nitrite ion concentrations were measured by differential pulse polarography as described earlier (Yilmaz and Somer, 2008) with minor modifications. Measurements were conducted in situ during the adsorption experiment. A PC-controlled POL150 polarograph, equipped with a MDE150 polarographic stand and three electrodes, was used. Ag/AgCl electrode was used as reference, while the counter electrode was a platinum sheet. The working electrode was a hanging mercury drop electrode (HMDE). All polarograms were measured using the parameters $E_{initial}$ −400 mv, E_{final} −1000 mv,



Scheme 1.

step duration 0.2 s, step amplitude 5 mv, purge time 30 s, pulse duration 20 ms and pulse amplitude 25 mv.

A stock solution of nitrite ions was freshly prepared every day by dissolving 1.499 g dried $NaNO_2$ in 100 mL distilled water and then diluting to 1000 mL. Nitrite ion intermediate solution (100 mg NO_2^-/L) was prepared by diluting 100.00 mL of the stock solution to 1.00 L with distilled water. The polarographic measurements were not affected by original solution pH values, due to dilution of the measured aliquot. To 5.00 mL of distilled water, placed in the polarographic vessel, were added 1.00 mL of reagent (0.10 M diphenylamine) and 0.40 mL nitrite ion solution. The diphenyl amine reagent solution was prepared by dissolving 0.169 g in 100.00 mL of (methanol 99% and concentrated acetic acid 99%) with volume ratio (1:1). **C**alibration curves were used in measuring the remaining nitrite ion concentrations in solutions by differential pulse polarography.

Table 2
Correlation between measured relative surface areas and nitrite ion uptake (after 60 min contact time) for different prepared AC systems. Measurements were made at room temperature, using 50 mL solution of nominal NO_2^- concentration (20 mg/L), and 0.30 g adsorbent.

Sample code	Relative surface area (m^2/g)	Nitrite ion removal[c] %	Nitrite ion up-take[c] (mg NO_2^-/g C)
OS	<100[a]	11.75	0.39
OSC	150[a]	6.75	0.23
H_3PO_4/450-AC	400[a]	13.5	0.45
$ZnCl_2$/450-AC	1480[a]	67.5	2.25
CAC	1000 m^2/g[b]	15.40	0.51

[a] Measurement based on acetic acid adsorption at 25 °C.
[b] From literature (Kaya et al., 2008).
[c] Measured after 60 min, using 0.30 g adsorbent in 50 mL solution, with nominal pH 4.0 at 25 °C.

3. Results and discussions

3.1. AC characterization results

AC samples prepared by different methods exhibited different surface morphologies, as depicted from SEM micrographs. Fig. 1 summarizes surface morphologies for different AC materials prepared here. Fig. 1a shows that the dried solid OS showed slightly textured surfaces, whereas Fig. 1b shows more textured surface for OSC. The H_3PO_4/450-AC, described here, showed higher porosity than the non-chemically activated counterpart, as observed from Fig. 1a–c. Fig. 1c shows a surface with no profound porosity for H_3PO_4/450-AC. This is contrary to other reported systems based on different agricultural wastes. Reffas et al. reported that highly porous surfaces were observed in H_3PO_4 activated carbons, at 450 °C temperature, from coffee grounds (Reffas et al., 2010). The difference between the two systems is presumably due to the nature of cellulosic materials present in coffee ground and olive solid wastes. Moreover, Reffas performed the activation under air, whereas inert atmosphere was used in this work. Under air, the carbonized charcoal undergoes oxidation and burning, which may wash it away, whereas under inert atmosphere such a burning process does not occur. The challenge in this work is to produce AC materials with high surface areas while avoiding charcoal burnout. The phosphoric acid examined here seems not a good activating agent for the stated objectives of this work.

The $ZnCl_2$/450-AC, Fig. 1d, showed more porous structure than the H_3PO_4/450-AC. Activation at higher temperatures, 600 or 750 °C did not cause significant enhancement in porosity, and was thus avoided for cost and energy saving purposes. A closer look at the SEM image for the $ZnCl_2$/450-AC shows that the solid has

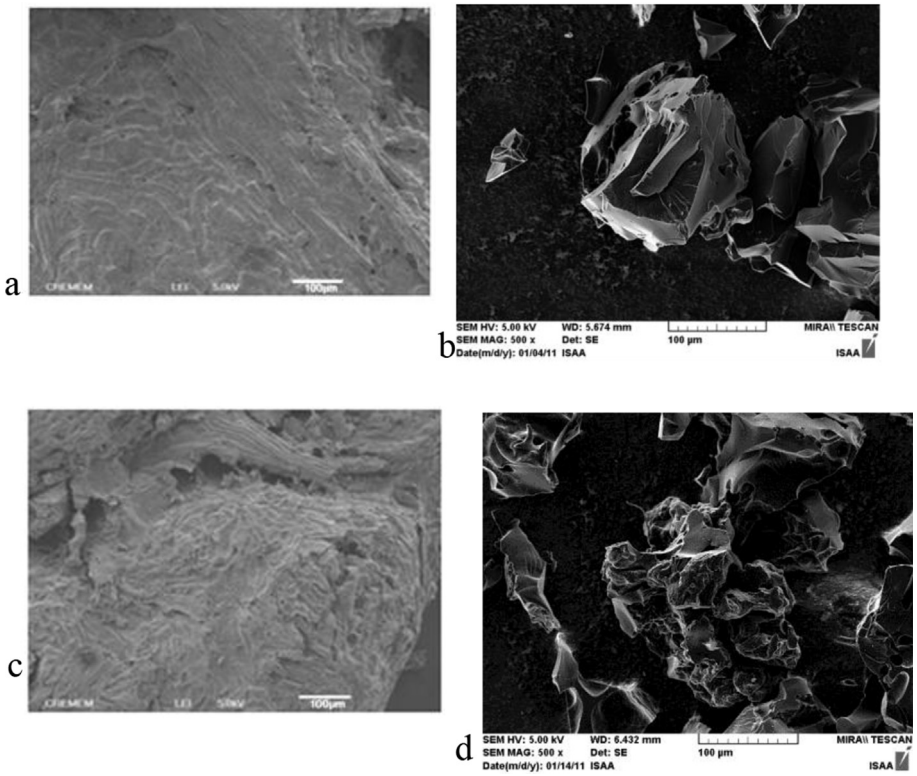


Fig. 1. SEM micrographs measured for a) OS; b) OSC; c) H_3PO_4/450-AC d) $ZnCl_2$/450-AC.

different types of pores with different parameters. Larger pores with ~10 μm in diameter exist together with smaller pores in the nanometer scale.

The relative surface area results, Table 2, are consistent with SEM micrographs. The OSC and OSC exhibited relatively low relative surface areas (~150 m^2/g). The H_3PO_4/450-AC showed higher relative surface area value ~400 m^2/g, and the $ZnCl_2$/450-AC exhibited much higher value 1480 m^2/g.

Based on surface porosity and relative surface area, $ZnCl_2$ seems to be more favorable agent over the H_3PO_4 for activation of carbon from olive solid waste, under the working conditions. Technically speaking, the $ZnCl_2$ agent was also more feasible to handle. The AC product resulting from $ZnCl_2$ activation was easier to purify, as the excess $ZnCl_2$ was easily removed by washing, whereas the H_3PO_4 was too difficult to remove due to its oily nature and strong adsorption onto the solid. This manifests the added value of using $ZnCl_2$ as activating agent. Collectively the results make activation using $ZnCl_2$ the method of choice in this work, and unless otherwise stated, the $ZnCl_2$/450-AC was used in this study. For comparison purposes, CAC samples were used in parallel. The FT-IR spectrum measured for the $ZnCl_2$/450-AC resembled that measured for the CAC, as shown in Fig. 2. Both spectra showed bands characteristic for O—H, C—H, C═C and C—O stretching frequencies, as reported earlier for activated carbons based on different materials (Al-Swaidan and Ahmad, 2011; Belgacem et al., 2013; Boonamnuayvitaya et al., 2005), as shown in Table 3.

Thermal gravimetric analysis (TGA) for bot $ZnCl_2$/450-AC and CAC showed similar behaviors, as shown in Fig. 3. Both compounds exhibited carbon mass lowering starting at 250 °C and reaching steady values above 700 °C. The lowering at ~100 °C is due to loss of moisture from the samples. The TGA pattern for the $ZnCl_2$/450-AC sample showed remaining stuff at above 800 °C due to remaining inorganic salts, presumably due to the $ZnCl_2$ activating agent itself.

Functional groups on the CAC and $ZnCl_2$/450-AC surfaces were determined by the Boehm acid-base titration method (Boehm, 1994). The results are shown in Table 4. The Table shows that the carboxylic acids are the dominant functional groups in both the CAC and the $ZnCl_2$/450-AC solid surfaces.

The pH values at zero point of charge (pH_{ZPC}) were also measured by known methods (Al-Degs et al., 2000). The values for

Table 3
FT-IR spectral characteristic bands observed for $ZnCl_2$/450-AC and CAC samples.

Wave number (cm^{-1})	Functional group
3500—4000	O—H stretching
2800—3000	C—H stretching
1600—1700	C═C (conjugated) stretching
1250	C—O stretching

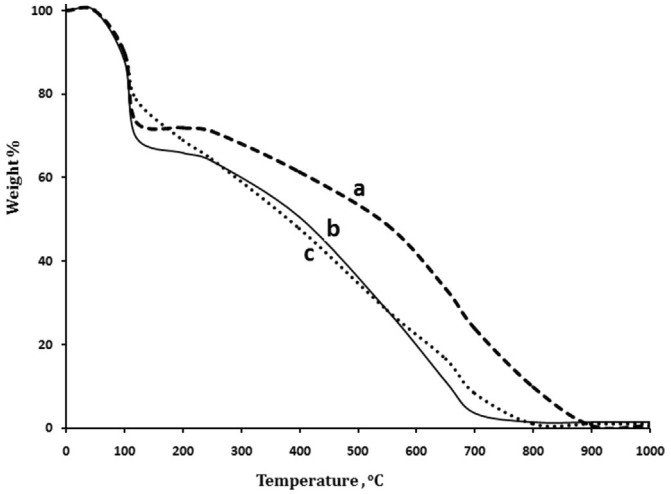


Fig. 3. TGA patterns observed for a) CAC, b) $ZnCl_2$/450-AC, and c) Non-Activated Carbon.

Table 4
Measured values of functional groups on the CAC and $ZnCl_2$/450-AC surfaces measured by the Boehm method.

AC type	Carboxylic (mmol/g)	Phenolic (mmol/g)	Lactonic (mmol/g)	Basic sites (mmol/g)
CAC	0.66	0.21	0.27	0.43
$ZnCl_2$/450-AC	1.19	0.23	0.31	0.24

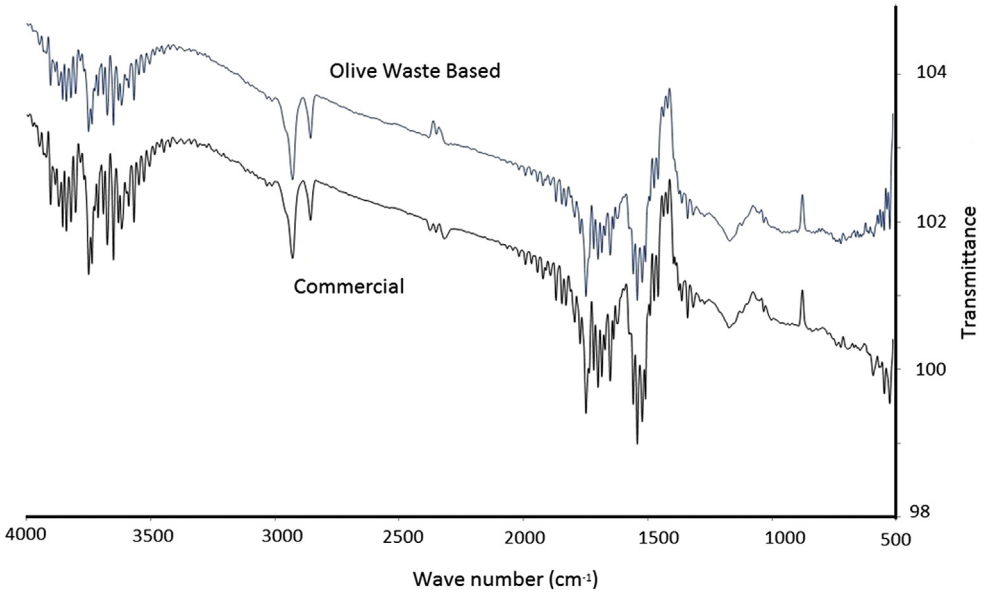


Fig. 2. FT-IR spectra measured for $ZnCl_2$/450-AC and CAC samples.

CAC and $ZnCl_2$/450-AC materials were 5.8 and 4.3, respectively.

3.2. Nitrite ion adsorption

The characterization results discussed above were further examined by adsorption study of the nitrite ion. The values of nitrite removal percent from originally contaminated nitrite aqueous solutions (20 mg/L) using a constant pH value at 25 °C, after 60 min, were calculated. Within the specified time, the $ZnCl_2$/450-AC was much more effective in removing the nitrite ions than either the H_3PO_4/450-AC or the OSC.

Nitrite ion uptake values are summarized in Table 2. The results show that adsorption was affected by particle size of the adsorbent. More nitrite ions were removed using powder carbon particles than using granular carbon. However, for comparison purposes with CAC, granular AC samples were used in adsorption study. The granular AC was also easier to recover by simple filtration. The granular AC materials were thus used throughout this work.

The results discussed above clearly indicate the higher ability of the $ZnCl_2$/450-AC to adsorb nitrite ions, than other counterpart carbons do, at least within a given period of time. This shows the feasibility of using the $ZnCl_2$-activated carbon, and unless otherwise stated, adsorption experiments described below were all performed using $ZnCl_2$/450-AC. Effects of different experimental parameters on nitrite ion adsorption behavior have been examined. For comparison purposes, the adsorption behavior of the prepared AC was investigated in parallel with CAC.

3.2.1. Adsorption profiles with time

Nitrite ion removal by $ZnCl_2$/450-AC and CAC is shown in Fig. 4. The Figure shows profiles of nitrite ions remaining inside the contaminated solutions with time, under the working conditions. In case of CAC, saturation was reached within 25 h, with no more than 25% removal of nitrite ions. In case of $ZnCl_2$/450-AC, adsorption continued to occur reaching more than 90% removal of nitrite ions after 25 h. The WHO stated maximum acceptable nitrite ion concentration to be 3 mg NO_2^-/L (Organization, 2004). The results show that using 5.0 g of $ZnCl_2$/450-AC per 1 L of highly pre-contaminated water (40 mg NO_2^-/L) can bring the nitrite level down to the WHO acceptable contamination levels, after 24 h treatment. This shows the feasibility of using $ZnCl_2$/450-AC in future large scale water purification strategies, which highlights the potential impact of this work in nitrite removal processes. Other activated carbons prepared here were uncompetitive with the $ZnCl_2$/450-AC, nor was the CAC.

3.2.2. Effect of pH

The effect of pH on nitrite ion adsorption, onto $ZnCl_2$/450-AC and CAC, was investigated. Fig. 5 shows that within 60 min contact time (before equilibrium), percentage removal of nitrite ion increased with lower pH and decreased with higher pH values. At each pH value, the AC prepared here was more efficient than the CAC, in adsorbing the nitrite ions.

The effect of pH is understood by changing the nature of the carbon surface with pH. At lower pH values, the solution contains more protons, which convert the carbon surface into the H-form. This favors adsorption of the negatively charged nitrite ions onto the surface. At higher pH values, the carbon surface releases the H^+ ions and holds negative charges which retard the nitrite ions and lower adsorption.

At lower solution pH values, the majority of nitrite ions are converted into the weak nitrous acid in a way of an equilibrium (Chang, 2010). Despite that, the nitrite ions/nitrous acid adsorb more at lower pH values as observed from the Figure. This means that the nitrite ions may be adsorbed in either free ionic form or in nitrous acid form. The H-form of the carbon surface may thus adsorb the nitrous acid via the oxygen atoms which carry partial negative charges.

The high adsorption of the AC in acidic media and low adsorption in basic media may impose limitation on using AC in nitrite removal studies. On the other hand, this could be advantageous by the fact that desorption and AC recovering strategies can be further investigated by shifting acid-base conditions in the solution.

3.2.3. Effect of temperature

The effect of temperature on nitrite ion adsorption onto $ZnCl_2$/450-AC and CAC was investigated. Fig. 6 shows how adsorption changes for both solid surfaces as temperature changes in the range 10–40 °C within 60 min contact time.

The Figure shows that removal of nitrite ions by both carbon materials increases with increased temperature. While the CAC showed only limited removal of nitrite ions at lower temperatures, the $ZnCl_2$/450-AC showed significant removal at such temperatures. This indicates the applicability of the prepared $ZnCl_2$/450-AC as adsorbent at different temperatures within the working conditions.

3.2.4. Kinetics of nitrite adsorption

Normally speaking, the adsorption mechanism depends on the type of adsorbent and on the adsorbate transfer processes (Uğurlu et al., 2007). In this work, three reported adsorption models were

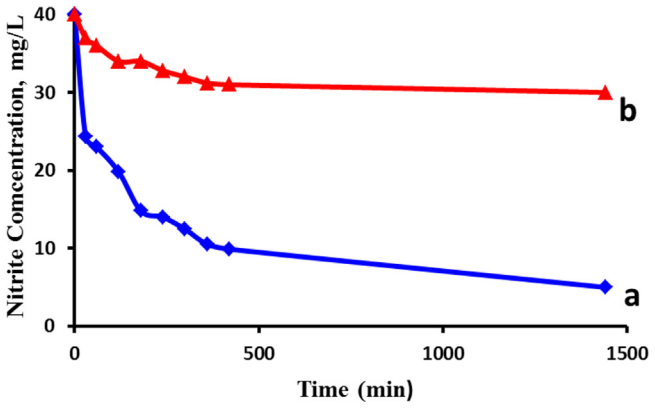


Fig. 4. Effect of contact time on the removal of nitrite ions (from 40 mg/L solution) by a) $ZnCl_2$/450-AC and b) CAC. Measurements were made using 0.25 mg solid/50 mL solution and initial pH 4, at 30 °C.

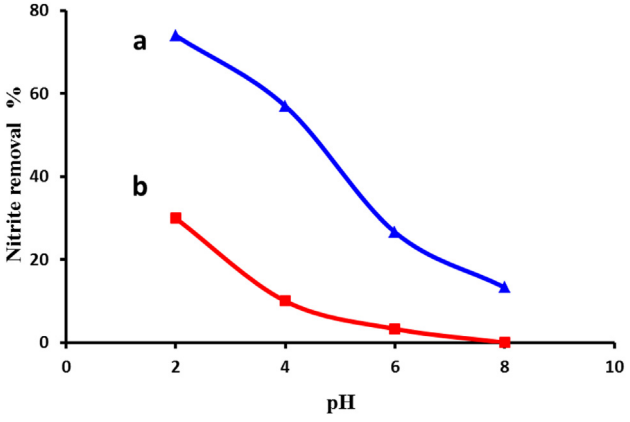


Fig. 5. Effect of pH on removal of nitrite ions (from solution 30 mg/L) by a) $ZnCl_2$/450-AC and b) CAC. Measurements were made using 0.30 g solid/50 mL solution at 25 °C, after 60 min contact time (before equilibrium).

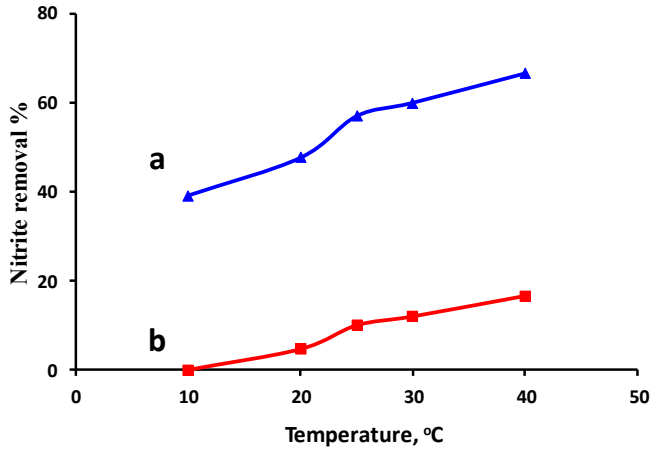


Fig. 6. Effect of temperature on removal of nitrite ions (from 30 mg/L solution) by a) $ZnCl_2$/450-AC and b) CAC. Measurements were made using 0.30 g solid/50 mL solution, at initial pH 4, after 60 min contact (before equilibrium).

tested, namely:

- The pseudo-first order model (Öztürk and Bektaş, 2004; Uğurlu et al., 2008, 2007; Yuh-Shan, 2004), Equation (1):

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}(q_e) - k_1(t/2.303) \quad (1)$$

- The pseudo-second order model (Öztürk and Bektaş, 2004; Uğurlu et al., 2008, 2007), Equation (2):

$$t/q_t \; 1/(k_2 q_e^2) + (1/q_e)t \quad (2)$$

- The intra-particle diffusion model (Tan et al., 2008; Tu et al., 2012), mathematically expressed as:

$$q_t = k_p t^{1/2} + A \quad (3)$$

where q_e and q_t (mg/g) are the amounts of adsorbate per unit mass of adsorbent at equilibrium and at time t (min), respectively; k_1 (min^{-1}) is the pseudo-first-order rate constant for adsorption, k_2 (g/mg min) is the pseudo-second-order rate constant of adsorption and k_p (mg/g $min^{1/2}$) is the rate constant of intra-particle diffusion, respectively; A is a parameter that tells about the thickness of the boundary layer (Kavitha and Namasivayam, 2007).

Linear plots were observed based on the pseudo-first-order and on the pseudo-second-order models for both $ZnCl_2$/450-AC and CAC. The measured parameter values are summarized in Table 5.

Table 3 shows that the correlation coefficient (R^2) values of both models are close to 1.00. In each adsorbent, the difference between the two models is pronounced in values of the calculated equilibrium nitrite concentration $q_{e(calc)}$. The Table shows that, unlike the pseudo-first-order model, the $q_{e(calc)}$ value for the pseudo-second-order model resembles the experimental value $q_{e(exp)}$. This applies to both adsorbents used. Therefore, the pseudo-second-order kinetic model is more suitable to describe the kinetics of adsorption of nitrite ions onto both solids. Chemisorption of the nitrite ions onto both adsorbents is presumably involved (Hanafiah et al., 2009; Ho and McKay, 1999; Tan et al., 2008). This is consistent with the fact that the adsorption (in 60 min) of nitrite ions increased with temperature, as shown in Fig. 6.

In order to envision the rate determining step, the intra-particle diffusion model (Kavitha and Namasivayam, 2007; Musapatika, 2010; Tan et al., 2008; Uğurlu et al., 2008, 2007; Wu et al., 2009) was investigated, based on Equation (3):

Linear plots for both $ZnCl_2$/450-AC and CAC were observed and the results are summarized in Table 6. According to the intra-particle diffusion model, a non-zero value for the intercept indicates that the rate of diffusion is limited by mass transfer across the boundary layer (Wu et al., 2009).

3.2.5. Adsorption isotherms

Fig. 7 shows experimental equilibrium adsorption isotherm for nitrite ions onto $ZnCl_2$/450-AC.

Langmuir and Freundlich isotherm models were both employed using Equations (4) and (5), respectively. Linear plots were observed in each case, and the values of the adsorption plot parameters are summarized in Table 7.

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (4)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g) at equilibrium, K_F is Freundlich constant, and n is an indicator for occurrence of adsorption process. K_F ((mg/g) (L/mg) $^{1/n}$) is related to adsorption capacity of the adsorbent.

The negative Langmuir isotherm parameters indicate the non-suitability of the model to explain adsorption process (Ramakrishna and Viraraghavan, 1997), whereas the Freundlich

Table 5
Pseudo-first-order and pseudo-second-order kinetic model parameters for nitrite ion adsorption onto $ZnCl_2$/450-AC and CAC. Measurements were made using 40 mg nitrite/L, and 0.25 g solid/50 mL in pH 4 solution at 30 °C.

Adsorbent	$q_{e\ (exp)}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (min^{-1}) 10^{-3}	$q_{e\ (calc)}$ (mg/g)	R^2	k_2 (g/mg min) 10^{-3}	$q_{e\ (calc)}$ (mg/g)	R^2
$ZnCl_2$/450-AC	7.00	3.68	4.32	0.98	2.56	6.71	0.99
CAC	2.00	5.07	1.66	0.98	4.23	2.20	0.98

Table 6
Intra-particle diffusion kinetic model parameters for nitrite adsorption onto $ZnCl_2$/450-AC and CAC. Measurements were made using nitrite ion solution (40 mg/L) and adsorbent (0.25 g/50 mL) with initial pH 4 at 30 °C.

Adsorbent	k_p (mg/g $min^{1/2}$)	R^2	A
$ZnCl_2$/450-AC	0.21	0.98	1.95
CAC	0.08	0.98	0.19

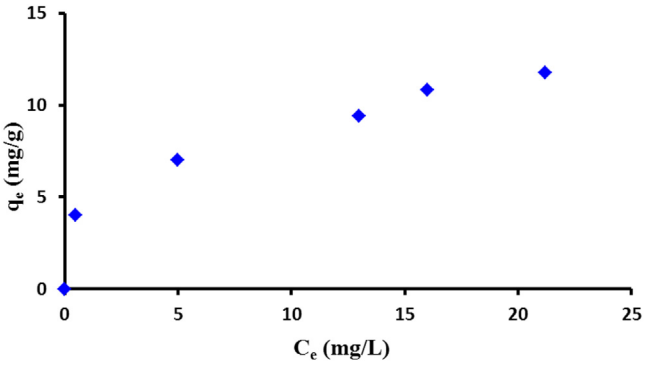


Fig. 7. Equilibrium adsorption isotherm of nitrite ions onto $ZnCl_2$/450-AC (0.25 g solid/50 mL) using initial pH 4 at 30 °C.

Table 7
Langmuir and Freundlich isotherm model parameters and correlation coefficients for nitrite adsorption onto $ZnCl_2$/450-AC. Measurements were made using adsorbent 0.25 g/50 mL solution with initial pH 4 at 30 °C.

Isotherm	Langmuir			Freundlich		
Adsorbate	Parameters			Parameters		
	Q_o (mg/g)	b (L/mg)	R^2	K_F ((mg/g) (L/mg)$^{1/n}$)	n	R^2
NO_2^-	−93.46	−0.013	0.74	3.89	2.78	0.99

model looks more appropriate by showing positive parameter values. The Freundlich isotherm parameters can be used in confirming the value of adsorption capacity, where adsorption increases as K_F values increase. The value of **n** being within the range 1–10 confirms suitability of the model for adsorption, as reported earlier (Öztürk and Bektaş, 2004).

Based on the kinetic results shown in Table 2, the values for adsorption capacity of $ZnCl_2$/450-AC and CAC were obtained for the batch system experiments, as shown in Table 8 (entries 4–5), with multi-layer adsorption based on Freundlich model. The Table shows value of adsorption capacity for nitrite onto $ZnCl_2$/450-AC and CAC samples, together with reported values for other materials (entries 1–5). The results indicate that $ZnCl_2$/450-AC has much higher adsorption capacity than the reported materials. An earlier report (Ho and McKay) stated an adsorption capacity of up to 50 mg nitrite per 1 g carbon cloth (which was pretreated with acidic media), however the adsorption capacity described therein could not be confirmed due to lack of description of experimental conditions. Packed column flow adsorption experiments (entry 6) indicate that the adsorption capacity for the $ZnCl_2$/450-AC is also higher than for other reported systems (entries 1–3 and 7). The lower adsorption capacity values measured in packed column adsorption experiments compared to the batch experiment systems are presumably due to insufficient time allowed for equilibrium to be achieved. This is because batch experiments were allowed to continue for more than 1500 min (Fig. 5) whereas the column flow experiments were only allowed for 130 min.

Collectively, the kinetic models and adsorption capacity results show that the $ZnCl_2$/450-AC described here is far more advantageous than earlier adsorbent systems. This shows the potential value of using such a material for future water purification strategies. Work is underway here to benefit from possible reversible adsorption to investigate multiple recycling of the AC adsorbent. Work is also underway to provide better characterization for the prepared AC material. Packed column flow study on the AC is also underway to find conditions for highest possible adsorption capacity.

Table 8
Comparison of nitrite specific adsorption capacity values on different materials.

Entry no.	Material	Nominal NO_2^- conc. (mg/L)	Adsorption capacity (mg/g)	Reference
1	Sepiolite	25	0.65	(Neşe and Ennil, 2008)
2	Powder activated carbon	25	1.17	(Neşe and Ennil, 2008)
3	Carbon cloth	–	0.828 (neutral)	(Afkhami, 2003)
4	$ZnCl_2$/450-AC	40	7.00	This work[a]
5	CAC	40	2.00	This work[a]
6	$ZnCl_2$/450-AC	40	3.65	This work[b]
7	CAC	40	1.85	This work[b]

[a] Batch adsorption experiments, using 0.25 g AC in 50 mL solution with initial pH 4 at 30 °C.
[b] Packed column flow experiments, using 1.00 g AC (3.0 cm long) and 200 mL solution (flow rate 1.5 mL/min) with initial pH 4 at 30 °C.

4. Conclusions

Activated carbon (AC) materials were prepared from olive solid wastes for the purpose of removal of nitrite ions from water. Chemical activation, using two different non-hazardous materials, H_3PO_4 and $ZnCl_2$, was investigated. The $ZnCl_2$ showed a product with high surface area and high adsorption capacity for nitrite ions, with the potential to bring the contaminant concentration to within acceptable limits. The $ZnCl_2$-activated AC showed much higher adsorption capacity than earlier reported materials. The results show the added value of using the proper activating agents to produce AC materials from olive solid waste, especially in olive tree-rich Mediterranean countries.

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References

Afkhami, A., 2003. Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: an approach to purification of water and waste-water samples. Carbon 41, 1320–1322.
Afkhami, A., Madrakian, T., Karimi, Z., 2007. The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions. J. Hazard. Mater. 144, 427–431.
Al-Degs, Y., Khraisheh, M., Allen, S., Ahmad, M., 2000. Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. Water Res. 34, 927–935.
Al-Swaidan, H.M., Ahmad, A., 2011. Synthesis and characterization of activated carbon from Saudi Arabian dates tree's fronds wastes. In: 3rd International Conference on Chemical, Biological and Environmental Engineering, pp. 25–31.
Alburquerque, J., Gonzálvez, J., Garcıa, D., Cegarra, J., 2004. Agrochemical characterisation of "alperujo", a solid by-product of the two-phase centrifugation method for olive oil extraction. Bioresour. Technol. 91, 195–200.
Angin, D., 2013. Production and characterization of activated carbon from sour cherry stones by zinc chloride. Fuel 115, 804–811.

Arnett, E.M., Cassidy, K.F., 1988. A thermochemical comparison of silica with other homogeneous and heterogeneous acids. Res. Chem. Intermed. 9, 27–64.
Ayyasamy, P., Rajakumar, S., Sathishkumar, M., Swaminathan, K., Shanthi, K., Lakshmanaperumalsamy, P., Lee, S., 2009. Nitrate removal from synthetic medium and groundwater with aquatic macrophytes. Desalination 242, 286–296.
Baccar, R., Bouzid, J., Feki, M., Montiel, A., 2009. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. J. Hazard. Mater. 162, 1522–1529.
Bagheri, N., Abedi, J., 2009. Preparation of high surface area activated carbon from corn by chemical activation using potassium hydroxide. Chem. Eng. Res. Des. 87, 1059–1064.
Belgacem, A., Belmedani, M., Rebiai, R., Hadoun, H., 2013. Characterization, analysis and comparison of activated carbons issued from the cryogenic and ambient grinding of used tyres. Chem. Eng. Trans. 32, 1704–1710.
Boehm, H., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 32, 759–769.
Boonamnuayvitaya, V., Sae-ung, S., Tanthapanichakoon, W., 2005. Preparation of activated carbons from coffee residue for the adsorption of formaldehyde. Sep. Purif. Technol. 42, 159–168.
Budinova, T., Ekinci, E., Yardim, F., Grimm, A., Björnbom, E., Minkova, V., Goranova, M., 2006. Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. Fuel Process. Technol. 87, 899–905.
Caturla, F., Molina-Sabio, M., Rodriguez-Reinoso, F., 1991. Preparation of activated carbon by chemical activation with $ZnCl_2$. Carbon 29, 999–1007.
Chang, R., 2010. Chemistry, tenth ed. Mc Graw Hill.
Cheremisinoff, P.N., Ellerbusch, F., 1978. Carbon Adsorption Handbook. Ann Arbor Science Publishers, Ann Arbor, Mich.
El-Hamouz, A., Hilal, H.S., Nassar, N., Mardawi, Z., 2007. Solid olive waste in environmental cleanup: oil recovery and carbon production for water purification. J. Environ. Manag. 84, 83–92.
Foo, K., Hameed, B., 2012. Mesoporous activated carbon from wood sawdust by K_2CO_3 activation using microwave heating. Bioresour. Technol. 111, 425–432.
Glasstone, S., Lewis, D., 1960. Elements of Physical Chemistry. van Nostrand, Princeton, NJ.
Hanafiah, M., Zakaria, H., Ngah, W.W., 2009. Preparation, characterization, and adsorption behavior of Cu (II) ions onto alkali-treated weed (Imperata cylindrica) leaf powder. Water, Air, Soil Pollut. 201, 43–53.
Ho, Y.-S., McKay, G., 1999. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.
Jimenez-Cordero, D., Heras, F., Alonso-Morales, N., Gilarranz, M.A., Rodríguez, J.J., 2014. Preparation of granular activated carbons from grape seeds by cycles of liquid phase oxidation and thermal desorption. Fuel Process. Technol. 118, 148–155.
Karthikeyan, S., Sivakumar, P., Palanisamy, P., 2008. Novel activated carbons from agricultural wastes and their characterization. J. Chem. 5, 409–426.
Kavitha, D., Namasivayam, C., 2007. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresour. Technol. 98, 14–21.
Kaya, Y., Gonder, Z., Vergili, I., Barlas, H., 2008. Removal of cetyltrimethylammonium bromide and sodium dodecylether sulfate by granular activated carbon. J. Sci. Industrial Res. 67, 249.
Kopac, T., Toprak, A., 2007. Preparation of activated carbons from Zonguldak region coals by physical and chemical activations for hydrogen sorption. Int. J. Hydrog. Energy 32, 5005–5014.
Lafi, W.K., 2001. Production of activated carbon from acorns and olive seeds. Biomass Bioenergy 20, 57–62.
Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Titirici, M.-M., Fühner, C., Bens, O., Kern, J., 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels 2, 71–106.
Liou, T.-H., 2010. Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation. Chem. Eng. J. 158, 129–142.
Martínez de Yuso, A., Rubio, B., Izquierdo, M.T., 2014. Influence of activation atmosphere used in the chemical activation of almond shell on the characteristics and adsorption performance of activated carbons. Fuel Process. Technol. 119, 74–80.
Martinez, M., Torres, M., Guzman, C., Maestri, D., 2006. Preparation and characteristics of activated carbon from olive stones and walnut shells. Industrial Crops Prod. 23, 23–28.
Melchert, W.R., Infante, C., Rocha, F.R., 2007. Development and critical comparison of greener flow procedures for nitrite determination in natural waters. Microchem. J. 85, 209–213.
Mestre, A.S., Bexiga, A.S., Proença, M., Andrade, M., Pinto, M.L., Matos, I., Fonseca, I.M., Carvalho, A.P., 2011. Activated carbons from sisal waste by chemical activation with K_2CO_3: kinetics of paracetamol and ibuprofen removal from aqueous solution. Bioresour. Technol. 102, 8253–8260.
Mikuška, P., Večeřa, Z., 2003. Simultaneous determination of nitrite and nitrate in water by chemiluminescent flow-injection analysis. Anal. Chim. Acta 495, 225–232.
Mishra, P., Patel, R., 2009. Use of agricultural waste for the removal of nitrate-nitrogen from aqueous medium. J. Environ. Manag. 90, 519–522.
Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., Nakanishi, T., 2004. Removal of nitrate-nitrogen from drinking water using bamboo powder charcoal. Bioresour. Technol. 95, 255–257.
Moussavi, G., Alahabadi, A., Yaghmaeian, K., Eskandari, M., 2013. Preparation, characterization and adsorption potential of the NH_4OH-induced activated carbon for the removal of amoxicillin antibiotic from water. Chem. Eng. J. 217, 119–128.
Musapatika, E.T., 2010. Use of Low Cost Adsorbents to Treat Industrial Wastewater. Faculty of Engineering and the Built Environment, University of the Witwatersrand.
Neşe, Ö., Ennil, K.T., 2008. A kinetic study of nitrite adsorption onto sepiolite and powdered activated carbon. Desalination 223, 174–179.
Okafor, P., Ogbonna, U., 2003. Nitrate and nitrite contamination of water sources and fruit juices marketed in South-Eastern Nigeria. J. Food Compos. Analysis 16, 213–218.
Olivares-Marín, M., Fernández-González, C., Macías-García, A., Gómez-Serrano, V., 2006. Preparation of activated carbon from cherry stones by chemical activation with $ZnCl_2$. Appl. Surf. Sci. 252, 5967–5971.
Organization, W.H., 2004. Guidelines for Drinking Water Quality. In: Recommendations, vol. 1. World Health Organization, Geneva.
Otten, D., Onorato, R., Michaels, R., Goodknight, J., Saykally, R., 2012. Strong surface adsorption of aqueous sodium nitrite as an ion pair. Chem. Phys. Lett. 519, 45–48.
Öztürk, N., Bektaş, T.E.l., 2004. Nitrate removal from aqueous solution by adsorption onto various materials. J. Hazard. Mater. 112, 155–162.
Pashley, R., Karaman, M., 2005. Applied Colloid and Surface Chemistry. John Wiley & Sons.
Petrov, N., Budinova, T., Razvigorova, M., Parra, J., Galiatsatou, P., 2008. Conversion of olive wastes to volatiles and carbon adsorbents. Biomass Bioenergy 32, 1303–1310.
Puziy, A., Poddubnaya, O., Martınez-Alonso, A., Suarez-Garcıa, F., Tascon, J., 2003. Synthetic carbons activated with phosphoric acid III. Carbons prepared in air. Carbon 41, 1181–1191.
Puziy, A., Poddubnaya, O., Martınez-Alonso, A., Suárez-Garcıa, F., Tascón, J., 2002. Synthetic carbons activated with phosphoric acid: I. Surface chemistry and ion binding properties. Carbon 40, 1493–1505.
Ramakrishna, K.R., Viraraghavan, T., 1997. Dye removal using low cost adsorbents. Water Sci. Technol. 36, 189–196.
Reffas, A., Bernardet, V., David, B., Reinert, L., Lehocine, M.B., Dubois, M., Batisse, N., Duclaux, L., 2010. Carbons prepared from coffee grounds by H_3PO_4 activation: characterization and adsorption of methylene blue and Nylosan Red N-2RBL. J. Hazard. Mater. 175, 779–788.
Rodríguez, G., Lama, A., Rodríguez, R., Jiménez, A., Guillén, R., Fernández-Bolanos, J., 2008. Olive stone an attractive source of bioactive and valuable compounds. Bioresour. Technol. 99, 5261–5269.
Rosas, J., Bedia, J., Rodríguez-Mirasol, J., Cordero, T., 2009. HEMP-derived activated carbon fibers by chemical activation with phosphoric acid. Fuel 88, 19–26.
Smâiések, M., éCernây, S., 1970. Active Carbon: Manufacture, Properties and Applications. Elsevier Pub. Co., Amsterdam and New York.
Sun, Y., Yue, Q., Gao, B., Li, Q., Huang, L., Yao, F., Xu, X., 2012. Preparation of activated carbon derived from cotton linter fibers by fused NaOH activation and its application for oxytetracycline (OTC) adsorption. J. Colloid Interface Sci. 368, 521–527.
Tan, I., Ahmad, A.L., Hameed, B., 2008. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. J. Hazard. Mater. 154, 337–346.
Tseng, R.-L., 2007. Physical and chemical properties and adsorption type of activated carbon prepared from plum kernels by NaOH activation. J. Hazard. Mater. 147, 1020–1027.
Tu, M., Huang, Y., Li, H.-L., Gao, Z.-H., 2012. The stress caused by nitrite with titanium dioxide nanoparticles under UVA irradiation in human keratinocyte cell. Toxicology 299, 60–68.
Uğurlu, M., Gürses, A., Açıkyıldız, M., 2008. Comparison of textile dyeing effluent adsorption on commercial activated carbon and activated carbon prepared from olive stone by $ZnCl_2$ activation. Microporous Mesoporous Mater. 111, 228–235.
Uğurlu, M., Gürses, A., Doğar, Ç., 2007. Adsorption studies on the treatment of textile dyeing effluent by activated carbon prepared from olive stone by $ZnCl_2$ activation. Color. Technol. 123, 106–114.
Velo-Gala, I., López-Peñalver, J.J., Sánchez-Polo, M., Rivera-Utrilla, J., 2014. Surface modifications of activated carbon by gamma irradiation. Carbon 67, 236–249.
Williams, P.T., Reed, A.R., 2006. Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste. Biomass Bioenergy 30, 144–152.
Wu, F.-C., Tseng, R.-L., Juang, R.-S., 2009. Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. Chem. Eng. J. 153, 1–8.
Yavuz, R., Akyildiz, H., Karatepe, N., Çetinkaya, E., 2010. Influence of preparation conditions on porous structures of olive stone activated by H_3PO_4. Fuel Process. Technol. 91, 80–87.
Yilmaz, Ü.T., Somer, G., 2008. Determination of trace nitrite by direct and indirect methods using differential pulse polarography and application. J. Electroanal. Chem. 624, 59–63.
Yuh-Shan, H., 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics 59, 171–177.