



A comparison study of peach stone and acrylonitrile-divinylbenzene copolymer based activated carbons as chromium(VI) sorbents

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ABSTRACT

Two activated carbons were produced by using two different precursor: peach stone and acrylonitrile-divinylbenzene copolymer. Peach stone based activated carbon was produced by single step steam activation at 800 °C, polymer based activated carbon was prepared in successive two stages; air oxidation at 300 °C and final carbonization at 850 °C under inert atmosphere. Produced carbons showed typical Type 1 nitrogen adsorption isotherms. Peach stone based activated carbon has 608 m²/g of surface area and 0.331 cm³/g of micropore volume, while polymer based carbon has 579 m²/g of surface area and 0.234 cm³/g of micropore volume. Boehm's titration results and Fourier transform infrared spectra indicated that the produced carbons possess acidic oxygen functionalities mainly in phenolic form. Polymer based activated carbon has 7.12 mmol of nitrogen/g because of the pyridine type groups in the main structure. The removal of Cr(VI) from aqueous solutions by activated carbon has been investigated as a function of solution pH. The maximum adsorption capacities were obtained at pH 2 in both cases and the maximum capacities were 143 mg/g, 83 mg/g and 150 mg/g for peach stone based, polymer based and commercial activated carbons, respectively.

The produced carbons could be regarded as potential adsorbents for efficient removal of Cr(VI) from aqueous media.

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1. Introduction

Chromium compounds, which are used in several industries such as leather, textile, metal plating, battery and pigments exist in two stable oxidation states as Cr(III) and Cr(VI). Cr(III) is relatively innocuous and is an essential trace element for living organisms. Because of its toxicity and carcinogenic nature, Cr(VI) compounds must be removed before discharging to the environment. The most common methods of Cr(VI) removal from aqueous system are: chemical precipitation, ion exchange, membrane processes, electro dialysis and adsorption [1]. Activated carbon is used as an adsorbent to remove some impurities from aqueous media depending on its specific surface area, pore structure and surface functionality. Although the use of activated carbons for removing chromium from wastewater has been received a great attention, the application in this field is not common because of limited adsorption capacity and high cost of commercial activated carbons.

Activated carbons can be produced from many carbonaceous materials available at low cost, both naturally occurring and synthetic [2]. However, commercial activated carbons are mainly

produced from wood, coal and coconut shell. It has been shown that activated carbons obtained from agricultural by-products can be favorable compared to conventional activated carbons with respect to their adsorptive properties, low cost and renewable sources [3]. Recently, various agricultural wastes such as fruit stones and shells have been used to develop lower cost activated carbons that have high adsorption capacity [4]. The important things are the availability and abundance of precursor. Peach stone is one of the most abundant agricultural waste products in Turkey from manufacturing peach juice. The world production of peach was 15,782,000 tons in 2006. Turkey is the fifth peach manufacturer in the world with the production of 485,000 tons [5]. Peach stones are usually used as an energy source, burned in the field or spilled into the environment in a non-controlled way. It is possible to convert this waste product to a valuable material, activated carbon, using different activation methods. The production process of activated carbon generally includes two separated steps: carbonization and activation. For saving energy and time these two steps were combined into one; consequently, peach stones were converted to an activated carbon by using one-step activation in this current work.

In contrast to activated carbons obtained from natural products, the pore structure of polymer-derived carbons can be better controlled by the choice of the precursor material i.e. its own porosity, chemical composition and pore size distribution plus choice of

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carbonization and activation conditions. Polymer-derived carbons display considerable adsorption capacity due to high specific surface area and are more stable and mechanically resistant than other types of carbonaceous materials. Also, polymers in the shape of beads received some attention due to good hydrodynamic properties of the resultant carbons in fixed bed/fluidized bed type separation applications.

The aim of the current study is to investigate the surface structural and functional properties of peach stone and polymer based activated carbons. In addition, chromium(VI) adsorption capacities of the produced carbons were also compared at different pHs. The kinetics and thermodynamics of chromium adsorption process will be the subject of the further studies.

2. Materials and methods

All chemicals used in this work were of analytical grade. Bituminous coal based granular commercial activated carbon (Chemviron Carbon, CPG-LF) was used for the comparison.

2.1. Preparation of precursors

Peach stones (PS) were obtained from a fruit juice factory in Bursa, Turkey. They were first washed with distilled water and dried in an oven at 105 °C for 24 h. Dried peach stones were crushed and sieved to particle size of 2–4 mm. Peach stones were pretreated by using successive alkali and acid solution in order to remove inorganic and humic substances from the main structure.

Acrylonitrile-divinylbenzene copolymer beads (AN/DVB) were produced using suspension polymerization method with hexadecane and toluene (1:9, w/w) as diluents. Polymerization mixture consisted in one-third from monomers and in two-thirds of inert diluents. The level of crosslinker was set at 40 wt.%. Full details of the polymerization were given in Ref. [6].

2.2. Production of activated carbons

The pyrolysis experiments were conducted in a horizontal quartz tube reactor with 6 cm of diameter and 55 cm of length. The reactor was heated using Protherm ASF tube furnace. The furnace had 25 cm length of heating area. Prepared peach stones were placed into the quartz reactor and heated to 800 °C at the rate of 5 °C/min under 500 mL/min nitrogen flow. Steam/nitrogen flow was passed through the reactor for 2 h at 800 °C. Approximately 50 mL/h steam was consumed during the activation period. After cooling to the ambient temperature in nitrogen atmosphere, they were rinsed with hot distilled water until neutral pH was obtained. Produced activated carbon (PS-AC) was stored in a desiccator after drying at 105 °C for 24 h.

AN/DVB copolymers were carbonized in two successive stages. In the first step, AN/DVB sample was oxidized under 100 mL/min air flow in a tube furnace. Tube furnace was heated with the rate of 50 °C/h. It was kept at 300 °C for 1 h and then 500 mL/min nitrogen flow was flushed to the oven for another 1 h at this temperature. In the second stage the temperature was raised to 400 °C and kept at this temperature for 4 h under nitrogen flow. Then the temperature was raised to 850 °C with the rate of 100 °C/h and the sample was kept at this temperature for 1 h. After cooling to the room temperature in nitrogen atmosphere, produced activated carbon (ANDVB-AC) was stored in a desiccator.

2.3. Characterization

2.3.1. Structural properties

N₂ adsorption measurements were performed using a Quantachrome Autosorb-1-C surface analyzer. The specific surface area,

N₂ adsorption isotherms and pore volumes were obtained from nitrogen adsorption data at 77 K. Prior to analysis, carbon samples were degassed at 200 °C for about 24 h. The density functional theory (DFT) model was used to determine the pore volumes. The surface area was calculated using Brunauer, Emmett, and Teller (BET) equation. All calculations were performed by the software provided with Quantachrome instrument.

The porous structure of produced carbons was visualized by using JEOL JSM-633SF model field emission scanning electron microscope.

2.3.2. Surface properties

The relative concentrations of acidic surface functional groups in carbons were determined by Boehm's titration with sodium hydrogen carbonate, sodium carbonate, and sodium hydroxide [7,8]. The concentrations of acidic sites were determined under the assumptions that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na₂CO₃ reacts with both carboxylic and lactonic groups; and NaHCO₃ is consumed by carboxylic groups only. Approximately 200 mg of dried carbon samples (size range 75–100 μm) were weighed in 50 mL glass conical dry flasks prior to the addition of 20 mL of 0.1 N NaOH, Na₂CO₃, NaHCO₃ solutions. The mixtures were shaken for 72 h at room temperature. The equilibrated solutions were filtered to remove adsorbent particles. Aliquots of 5 mL were titrated with a 0.1 N volumetric standard solution of HCl using methyl red as indicator. While the nature of the acidic surface sites is quite well understood, the origin of surface basicity is still under discussion [7]. Carbon samples were neutralized with a 0.1 N HCl as above and titrated with a 0.1 N volumetric standard solution of NaOH to determine total basic groups. All experiments were performed in duplicate.

The results of Boehm's titration were supported by Fourier transform infrared spectrum (FTIR). Analysis was performed with a Unicam Mattson 1100 model spectrometer using carbon samples dispersed in KBr-pellets.

Potentiometric titration data for the adsorbents were obtained using a method described by Helfferich [9]. Twenty carbon samples (containing 75 mg each, with particle size <45 μm) were weighed in 50 mL glass conical flasks. Variable amounts of 0.1 N sodium hydroxide (from 0.1 to 4.5 mL) and 0.1 N hydrochloric acid (from 0.1 to 4 mL) were added to adjust the pH. A 10 mL of 0.1 N NaCl solution was added to each flask to maintain a high background electrolyte solution. A total batch volume of 15 mL was prepared by adding distilled water to maintain the constant ratio of solution volume to sorbent weight. The samples were stirred for 72 h at room temperature to allow them to reach equilibrium. The initial (before the addition of adsorbent) and final pHs were measured for each sample using a WTW Inolab Level 1 pH meter. Basic titration data were transformed into proton binding isotherms using a proton balance equation and a theoretical blank reference. The obtained curves are positive for the proton binding process and negative for proton release.

The electrophoretic mobility of these equilibrated samples was also measured using a Malvern Instruments Zetasizer 3000HSA. Samples of the suspension were collected in plastic syringes and injected directly into the electrophoresis cell. Zeta potential was measured three times for each flask to provide an average reading.

Elemental analysis of the samples was carried by VarioEL III CHNS elemental analyser and nitrogen content of them was determined with Kjeldahl method by using a Buchi instrument.

2.3.3. Surface hydrophobicity

Hydrophobic bonding comes from the strong tendency of water molecules to associate with each other by hydrogen bonding. Hydrophobic bonding plays an important role in adsorption process. Carbon surface without any surface functional groups at

all, shows hydrophobic properties and cannot allow approaching water molecules to the surface. Increasing number of oxygen containing surface functional groups decreases hydrophobicity of carbon surface. The surface hydrophobicity of carbon materials can be determined by water adsorption. Water adsorption experiments were performed at two different constant partial vapour pressures at 22 °C. Partial vapour pressures were provided by using 50% and 10% of H₂SO₄ as 7.0972 and 19.1464 mm Hg, respectively [10]. 1 g of each activated carbon, which was dehydrated at 105 °C for a night, was weighed in plates. The plates were put into the desiccators containing each a 100 mL of H₂SO₄ solution. Water adsorbed by carbons was determined by weighing the plates.

2.4. Chromium(VI) adsorption

Chromium(VI) adsorption experiments were carried out by agitating 2–60 mg of activated carbon samples with 50 mL of Cr(VI) solution of 30 mg/L at pH from 2 to 8 at room temperature in orbital shaker. Synthetic chromium solution was prepared by dissolving potassium dichromate in distilled water. The pH of the solution was measured regularly using WTW Inolab Level 1 pH meter and kept constant by adding HCl and NaOH solutions during the batch sorption experiments. The equilibrium was obtained when there is no pH change of the solution.

Equilibrium Cr(VI) concentrations were determined at 540 nm wavelength by using Analytic Jena Specord 40 and JASCO V-530 UV Spectrophotometer after complexing with diphenylcarbazide at acidic medium [11].

Cr(VI) adsorption capacities were calculated by using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where q_e is adsorption capacity ($\text{mg}_{\text{Cr(VI)}}/\text{g}_{\text{activated carbon}}$), C_0 and C_e are the Cr(VI) initial and equilibrium concentrations (mg/L), respectively, V is the volume of the Cr(VI) solutions and m is the weight of activated carbon (g). Adsorption isotherms were obtained by plotting adsorption capacities with respect to equilibrium concentrations.

3. Results and discussion

3.1. Characterization

3.1.1. Structural properties of activated carbons

Nitrogen adsorption–desorption isotherms of the produced carbons are shown in Fig. 1. Both nitrogen adsorption isotherms are Type I, demonstrated highly microporous structure of the carbons [12]. As can be seen from Fig. 1 peach stone based activated carbon adsorbed higher amounts of nitrogen than polymer based carbon.

The surface area and pore structure of porous materials are extremely important when they are applied in sorption processes since this is where chemisorption and/or physisorption occurs. Table 1 shows specific surface area and pore volume of produced

Table 1
Surface area and pore volume of the samples.

Sample	Product yield (%)	Surface area (m^2/g) ^a	Total pore volume (cm^3/g) ^b	Micropore volume (cm^3/g) ^b
PS-AC	17	608	0.341	0.331
AN/DVB	82	70	0.143	0.026
ANDVB-AC	46	579	0.300	0.234
CPG-LF	–	693	0.351	0.318

^a BET method.

^b DFT method.

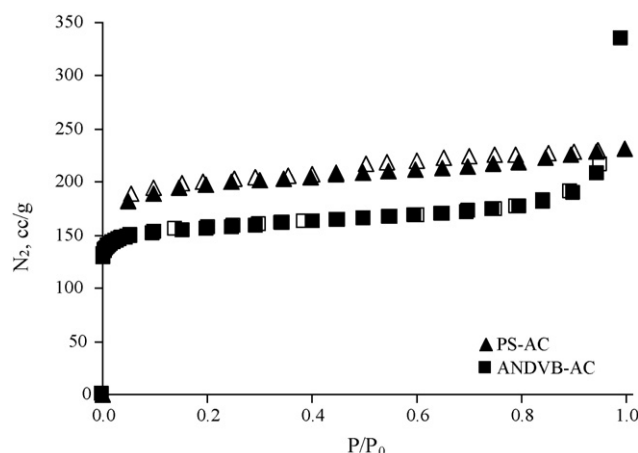
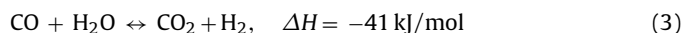
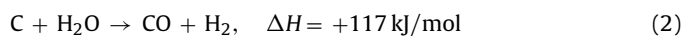


Fig. 1. Nitrogen adsorption–desorption isotherms.

samples with the product yield values. Both activated carbons have relatively high surface area and pore volume that can be compared with commercial carbon, CPG-LF. Peach stone based activated carbon has slightly higher surface area ($608 \text{ m}^2/\text{g}$), total pore volume ($0.341 \text{ cm}^3/\text{g}$) and micropore volume ($0.331 \text{ cm}^3/\text{g}$) than polymer based one ($579 \text{ m}^2/\text{g}$, $0.300 \text{ cm}^3/\text{g}$, and $0.234 \text{ cm}^3/\text{g}$, respectively). Additionally, its microporosity (97%) is also higher, even higher than that of commercial one. However, product yield of PS-AC (17%) is low compared with ANDVB-AC (46%). This can be attributed to the result of steam activation of peach stone. Carbon on main lattice reacts with steam according to the following reactions which is caused pore formation.



As can be seen from Table 1, the surface area and micropore volume of AN/DVB copolymer was increased from $70 \text{ m}^2/\text{g}$ and $0.026 \text{ cm}^3/\text{g}$ to $579 \text{ m}^2/\text{g}$ and $0.234 \text{ cm}^3/\text{g}$, respectively, with the carbonization. Hence, macroporous AN/DVB copolymer was successfully converted to microporous activated carbon, ANDVB-AC.

Scanning electron microscopy was used to visualize the surface morphology of produced carbons. Fig. 2 shows the SEM images of PS-AC and ANDVB-AC indicating the presence of microporous structure. However, different surface morphology of both carbons can be clearly observed from the SEM images. The peach stone based activated carbon has more irregular surface morphology compared to polymer based one. ANDVB-AC shows a spongy structure, the surface of PS-AC is like a honeycomb. The spherical shape of the AN/DVB was preserved after activation, consequently, polymer based activated carbon has mostly spherical shape type. The SEM images of ANDVB-AC clearly showed that the quite smooth surface of AN/DVB was considerably destroyed with the activation.

3.1.2. Surface properties of activated carbons

According to Boehm's titration results, both carbon samples possess acidic oxygen functionalities, mainly in the form of phenolic groups (Table 2). This result can be interpreted as a consequence of the gas phase oxidation. Shen et al. [13] demonstrated that the gas phase oxidation causes an increase in hydroxyl and carbonyl surface functional groups. A number of carboxyl groups ($-\text{COOH}$) were also determined on the surface of ANDVB-AC sample but not in the case of PS-AC. In addition, while peach stone based activated carbon has an equal amount of total acidic and basic functional groups, polymer based carbon is significantly acidic. It is accepted that the acidic or basic character of activated carbon depends on its preparation and treatment conditions. Thermal treatment at

Table 2
Concentration of functional groups on the surface of carbon samples.

Sample	Carboxylic groups (meq/g)	Lactonic groups (meq/g)	Phenolic groups (meq/g)	Acidic groups (meq/g)	Basic groups (meq/g)
PS-AC	UDL	0.0620	0.2540	0.3160	0.3190
ANDVB-AC	0.0976	0.0036	0.7789	0.8802	0.4918
CPG-LF	0.1572	UDL	0.5193	0.6765	0.1848

UDL: under detection limit.

high temperature (800–1000 °C) gives activated carbons with basic character which are known as H-type carbons. Although both carbons are produced at elevated temperature, polymer based carbon has acidic character. This can be attributed to the air treatment of AN/DVB copolymer at 300 °C. Air oxidation causes an increase in oxygen containing functional groups.

Although the nature of the acidic surface sites is quite well understood, the origin of surface basicity is still under discussion [8]. Delocalized π electrons on the edge of graphene layers of carbon can be responsible for this basic character. Boehm [8] stated that the basicity of delocalized π electrons is relatively weak. Furthermore, oxygen containing groups such as quinone, diketone, chromene and γ -pyrones may also cause this basic sites [14]. The pyridine type of nitrogen-containing groups also significantly contributes to the basicity of ANDVB-AC. Marsh and Rodriguez-Reinoso [14] informed that increasing the nitrogen content of the graphene layers considerably enhances their basicity. However, one should keep in mind that only the functional groups having pK values between 3.5 and 10.5 can be determined by this method since water shows buffering effect at very high and very low pH values [8].

The FTIR spectra of the obtained carbon samples are shown in Figs. 3 and 4. There are peaks at about 3400 cm^{-1} ,

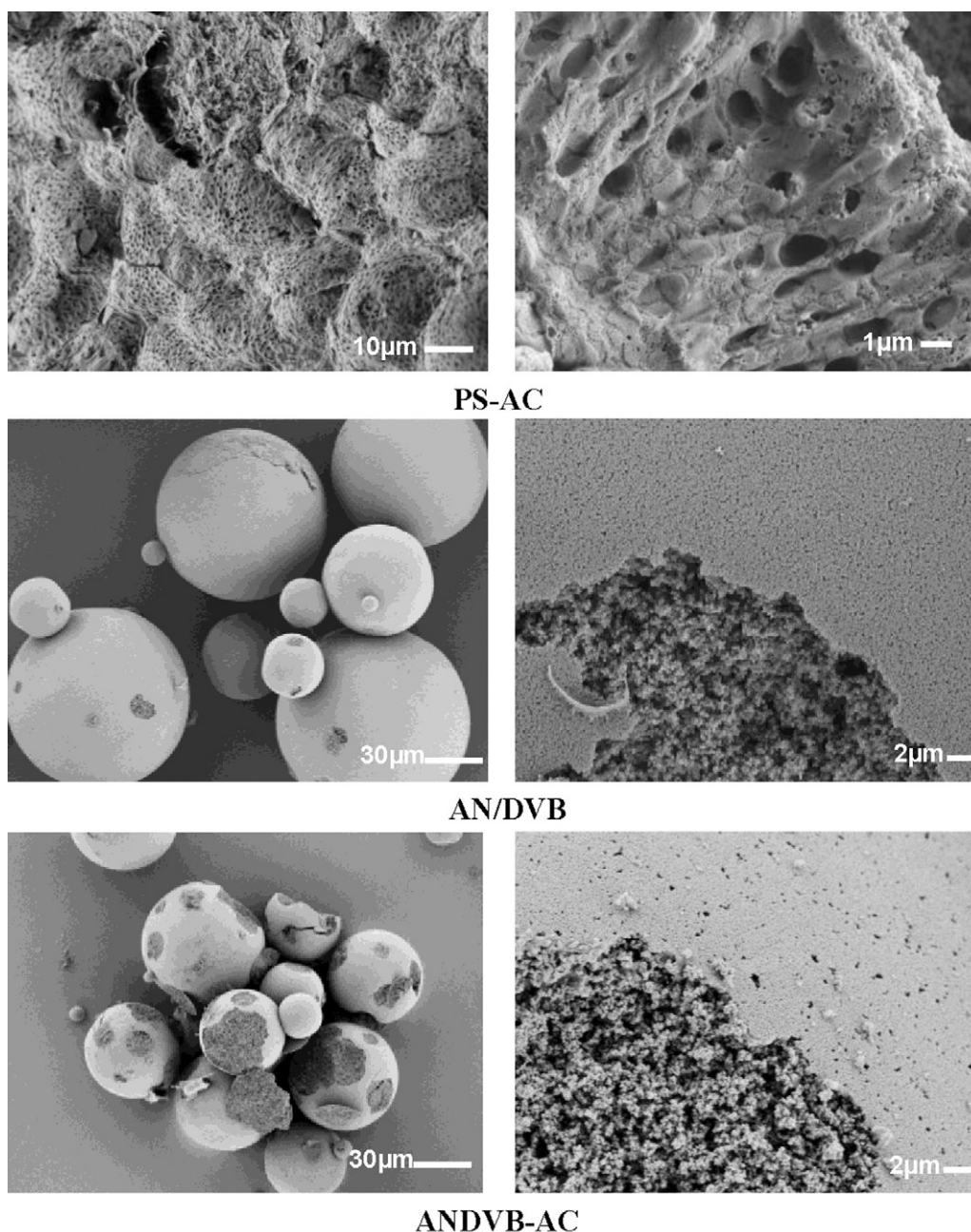


Fig. 2. SEM images of the produced samples.

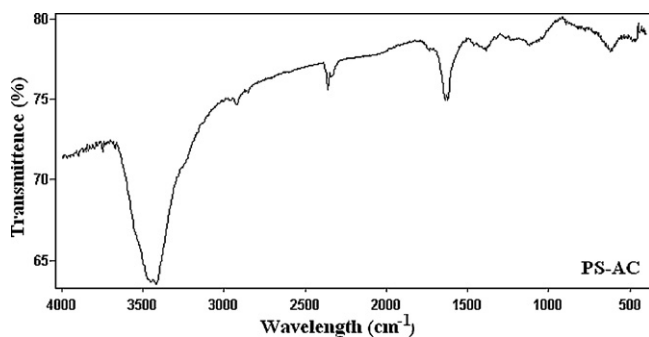


Fig. 3. FTIR spectra of peach stone based activated carbon.

2900 cm^{-1} , 2350 cm^{-1} , 1600 cm^{-1} , 1700 cm^{-1} , 1350–1400 cm^{-1} , and 1100–1200 cm^{-1} wavelengths (Figs. 3 and 4b). The band in the region of 3400 cm^{-1} is assigned to the O–H stretching vibrations of the functional groups such as alcohols and phenols [13,15–17]. On the other hand, it should be taken into consideration that the adsorbed water can affect the transmittance in this region.

The broad peak displayed shoulders at about 2900 cm^{-1} represents C–H stretching of methyl and methylene groups [15] or alkyl groups such as $-\text{CH}_3$, $=\text{CH}_2$ and $-\text{CH}_2\text{CH}_3$ [16]. The band at 2350 cm^{-1} is caused by $\text{C}\equiv\text{C}$ stretching vibration. Although the peak observed by many researchers at about 1600 cm^{-1} has not been interpreted exactly [18], some researchers reported that the C=C stretching vibration in aromatic ring can be responsible for this band for the most carbonaceous materials [13,15,16–19]. The C=O stretching vibration at 1700 cm^{-1} can be discriminated in few samples. In some cases, very broadband was observed between 1600 cm^{-1} and 1700 cm^{-1} that can be explained as overlapping of C=C and C=O stretching peaks. In addition, many functional groups can show absorption peak in this region like qinonic (1550–1680 cm^{-1}), carboxylic (1665–1760 cm^{-1}) and lactones (1675–1790 cm^{-1}). While the bands in the region of

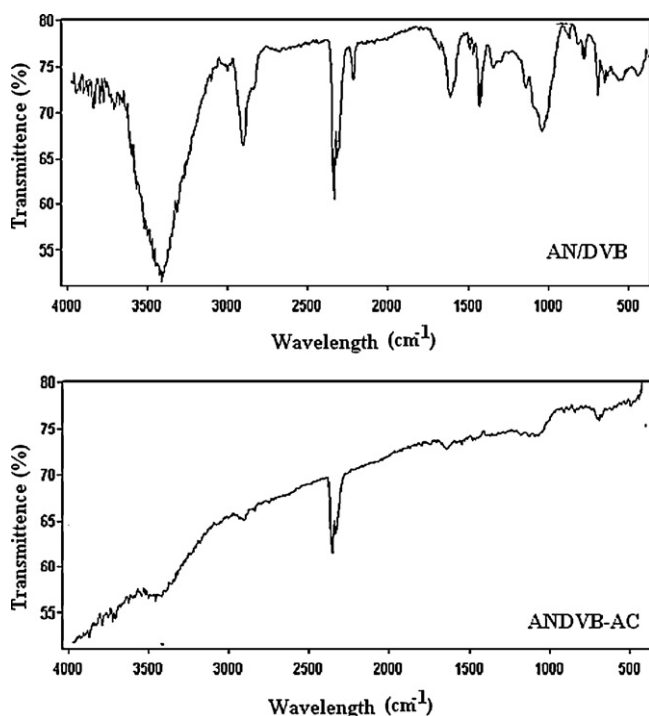


Fig. 4. FTIR spectra of AN/DVB and polymer based activated carbon.

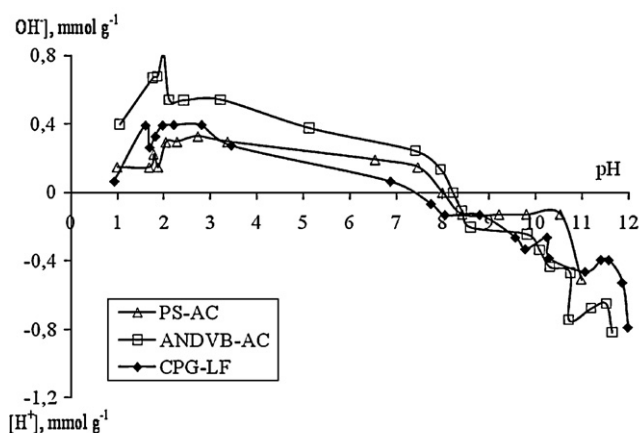


Fig. 5. Proton binding curves of carbon samples.

1350–1400 cm^{-1} can be assigned to carbonates, carboxyl carbonates and lactones, the small peaks between 1100 cm^{-1} and 1200 cm^{-1} can represent alcohols, C–H in ether, C–OH and O–H stretching in phenolic groups [13,17,19].

As can be seen in Fig. 4, most of peaks on FTIR spectrum of AN/DVB copolymer disappeared as a result of carbonization at high temperature. The band at 2200 cm^{-1} is caused by the nitrile groups ($\text{C}\equiv\text{N}$) in the structure of AN/DVB. This peak is not observed on the FTIR spectra of activated carbon, ANDVB-AC. During the production process of activated carbon, nitrile groups should have been converted to pyridine groups as a result of air oxidation, as expected. The band at around 1400 cm^{-1} represents C=N stretching of pyridine group.

The proton binding curves obtained from potentiometric titration depicted in Fig. 5, which indicate the presence of functional groups on the activated carbon surface. Although the shape of proton binding curves measured for both carbons (PS-AC and ANDVB-AC) are very smooth until pH about 7.5, the curves show significantly decaying tendency after this pH. This sharp falls are explained as a result of proton dissociation of phenolic groups. Strelko et al. [20] suggested that carboxylic groups dissociate in the pH interval 3–6 and phenolic groups dissociate above this pH. Due to the fact that the produced activated carbons have no or very small amount of carboxyl groups, the samples do not show considerable proton dissociation in the pH range of 3–6. The results obtained from pH titration analysis are in agreement with the results of Boehm titration.

The crossover point with the pH axis on the curves is the point where the anion and cation exchange are in equilibrium. This point is known as point of zero charge (PZC) and the surface of activated carbons are positively charged at pH values below the PZC. The crossover point of polymer and peach stone based activated carbons are located at about pH 8.2 and 8.0, respectively. H-type carbons, which are produced at high temperature, adsorb H^+ ions from water and exhibit positive surface charge [21]. The possible reactions which occur with increasing pH on the surface can be expressed as follows [22]:



These surface hydroxyl groups are called protonated, neutral and ionized, respectively. The activated carbon surface is protonated until pH_{PZC} and show great interest to the anions because of the electrostatic attraction. After pH_{PZC} value, proton dissociation from the surface occurs, consequently, deprotonated surface attracts to the cations. It can be concluded

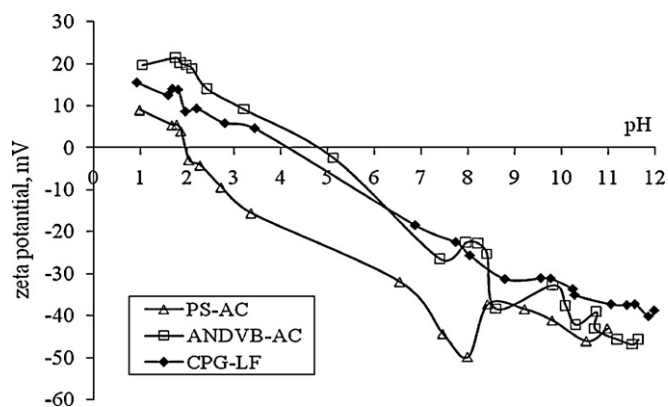


Fig. 6. Zeta potential measurements of carbon samples.

Table 3
Elemental compositions of the produced samples.

Sample	C (%)	H (%)	O (%)	N (%)	N (mmol/g) ^a
Peach stone	50.04	6.13	43.65	0.215	0.40
PS-AC	93.18	0.94	5.67	0.215	0.11
AN/DVB	79.76	6.86	2.02	11.36	7.12
ANDVB-AC	82.29	1.38	11.85	4.485	3.35

^a Measured by Kjeldahl method.

that both samples have positive surface charge density and are able to attract anions and would therefore promote the adsorption of the negatively charged chromium species in the solution.

Fig. 6 shows the zeta potential of the carbons as a function of pH. Zeta potential values of both carbons are decreasing to the negative values with pH. The pH value at the zero zeta potential is often called the isoelectric point (IEP) of the interface [20,23]. This parameter is very important to characterize the electrokinetic behaviour of a solid–liquid interface. The IEP values for PS-AC and ANDVB-AC are 1.9 and 4.8, respectively. A fresh H-type carbon generally has IEP value at about pH 7. The IEP value can shift to the lower pHs due to the atmospheric exposure over an extended period of time which is indicative of an L-type conversion [24].

Elemental compositions of the raw materials and activated carbons are presented in Table 3. The C percentages of both materials were increased with activation. This is much higher in case of peach stone than of ANDVB. Oxygen content of peach stone significantly decreased from 43.65% to 5.67% with activation by steam at high temperature. However, O contents of AN/DVB increased from 2.02% to 11.85% because of air oxidation. This is in agreement with the Boehm titration results. High N content is arisen from the nitrile groups (C≡N) presence in the polyacrylonitrile structure. During the high temperature treatment of AN/DVB to produce activated carbon, while some of these nitrile groups were converted to pyridine type groups, some of them removed from the structure as HCN.

3.1.3. Surface hydrophobicity of activated carbons

As can be seen from Table 4, water adsorption capacities of both activated carbons are sufficiently high. Even the amount of sur-

Table 4
Water adsorption capacity of produced carbon samples.

Partial vapour pressure (mm Hg)	PS-AC	ANDVB-AC
	Water adsorption capacity (mg/g)	
7.0972	157	145
19.1464	233	177

face functional groups of polymer-derived carbon is higher than peach stone based one, its water adsorption capacity is lower. It is well known that hydrophobicity of carbon decreases with surface functional groups [25], so, higher water adsorption capacity can be explained by higher pore volume of PS-AC. As a conclusion, it can be said that both activated carbons have sufficiently hydrophilic surface to allow approaching adsorbate ions hydrated by water molecules.

3.2. Cr(VI) adsorption results

Experimental Cr(VI) adsorption isotherms of activated carbons are shown in Fig. 7. All isotherm curves show typical Type 1 shapes according to IUPAC classification at pH 2 and 4. As can be seen from Fig. 7, while the capacity of peach stone based activated carbon is similar to commercial activated carbon at pH 2, polymer based carbon shows relatively low sorption capacity. This higher sorption is probably due to the highly microporous structure of PS-AC carbon in contrast with that of ANDVB-AC. Moreover, when acidic and basic surface functional groups are evaluated together (Table 2), ANDVB-AC has acidic character, which prevents approaching hydrogen chromate anions to the carbon surface at the studied pH range. One should also keep in mind that ANDVB-AC has more hydrophobic structure compared to PS-AC carbon (Table 4).

The differences between the capacities of two carbons (PS-AC and CPG-LF) and ANDVB-AC are significant at pH 2 but this difference decreases with pH. It means that decreasing of sorption capacity with raising pH is significant for PS-AC and CPG-LF but not for ANDVB-AC. Magnitudes of the capacity falling from pH 2 to 6 are about 66%, 64% and 48% for CPG-LF, PS-AC and ANDVB-AC, respectively. In respect of point of zero charge for all carbons (Fig. 5) are higher than studied pHs, all functional groups on the surface are non-dissociated. These groups are protonated throughout the [H]⁺ rich region, that is at low pH. If only interaction between protonated surface and chromium was responsible for sorption, according to electrostatic attraction, it would be expected to obtain similar capacity fall for all carbons with raising pH. Consequently, it can be concluded that electrostatic attraction is predominated for PS-AC and CPG-LF, but not for ANDVB-AC. There must be another process which is more effective than electrostatic attraction for the case of ANDVB-AC, like complex formation between hydrogen chromate and pyridine groups.

Cr(VI) exists as chromate ion (CrO₄²⁻) at pHs above 6.5. When studied at pH 8, the isotherm shapes are different and uptake capacities are very low (Fig. 7d). This could be explained as competitiveness between chromate and hydroxyl ions. Additionally, a chromate ion needs two active sites because of two minus charges of it.

It can be seen from Fig. 7, maximum Cr(VI) sorption capacity was obtained as 83 mg/g and 143 mg/g for polymer based and peach stone based activated carbon at pH 2, respectively. There are a lot of study about Cr(VI) adsorption onto activated carbon in the literature but only some of them show considerably high sorption capacities. Owlad et al. [26] obtained maximum 20 mg/g Cr(VI) adsorption capacity with polyethyleneimine impregnated palm shell based activated carbon. Acharya et al. [27] prepared activated carbon from tamarind wood with zinc chloride to adsorb Cr(VI). They obtained maximum adsorption capacity of 28 mg/g at low pH. Hamadi et al. [28] prepared activated carbon from waste tyres and saw dust by CO₂ activation. Their Cr(VI) adsorption capacities were 30 mg/g and 25 mg/g at pH 2 for waste tyre based and saw dust based carbon, respectively. Selomulya et al. [29] used different types of activated carbons which have higher than 1100 m²/g BET surface areas. They obtained 88 mg/g, 107 mg/g, 102 mg/g Cr(VI) adsorption capacities at pH 2 for wood based, coconut based and dust coal based activated carbons, respectively. Demiral et al. [30]

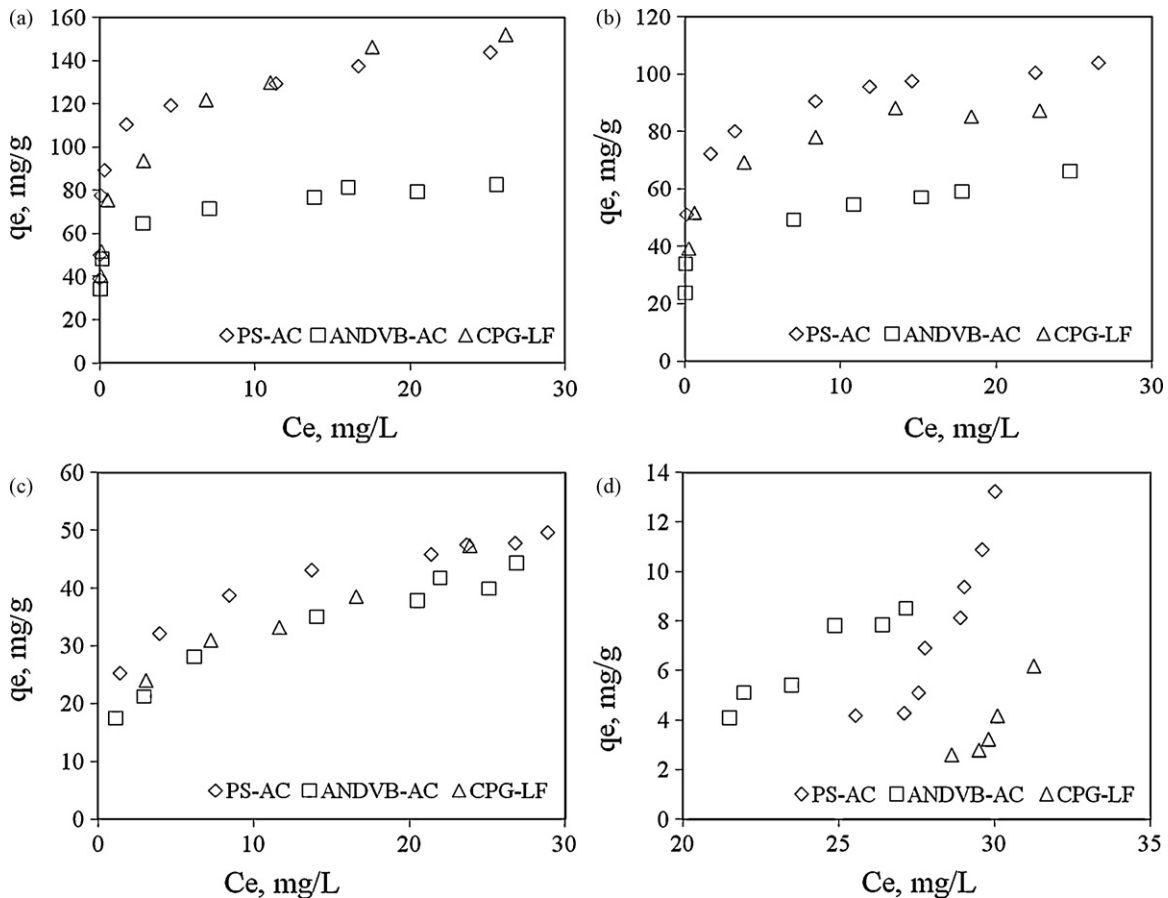


Fig. 7. Cr(VI) adsorption isotherms for PS-AC, ANDVB-AC and CPG-LF [(a) at pH 2, (b) at pH 4, (c) at pH 6, and (d) at pH 8].

prepared activated carbon from olive bagasse by steam activation, consequently, 718 m²/g activated carbon which has about 100 mg/g Cr(VI) adsorption capacity at pH 2 was obtained. Khezami and Chapart [31] tested KOH based and H₃PO₄ based activated carbon for adsorption of Cr(VI). They obtained maximum capacities at pH 3 as 160 mg/g and 100 mg/g for KOH based and acid based activated carbon, respectively. Kobya [32] obtained maximum 170 mg/g Cr(VI) adsorption capacity at pH 1 using hazelnut based activated carbon. Some of the activated carbons show low Cr(VI) sorption capacities (<12 mg/g), even if they have considerably high surface areas [33–36]. The reason could be the surface functionality of these carbons. Overall, comparing to the other works the produced activated carbons in this study have considerably high Cr(VI) sorption capacities which are capable to compete to the others.

Fig. 8 shows the Cr(VI) removal percentage which were obtained by using 20 mg activated carbon and 50 mL of 30 mg/L Cr(VI) solution. It is clear that while almost all Cr(VI) was removed with PS-AC and CPG-LF at pH 2, only 90% of Cr(VI) could be removed by ANDVB-AC at the same pH. Cr(VI) sorption capacity of carbon samples was strongly dependent on pH of the solution. The maximum Cr(VI) adsorption capacity was found at pH 2 for both activated carbons and it was decreased with increasing pH as observed by several workers [27–33,37–39]. The high Cr(VI) sorption capacity at low pHs could explain that the electrostatic attraction between positively charged groups of carbon surface and HCrO₄⁻ ions. Cr(VI) sorption capacity was decreased due to the decreasing electrostatic attraction and competitiveness between HCrO₄⁻ anions and OH⁻ ions at increased pH.

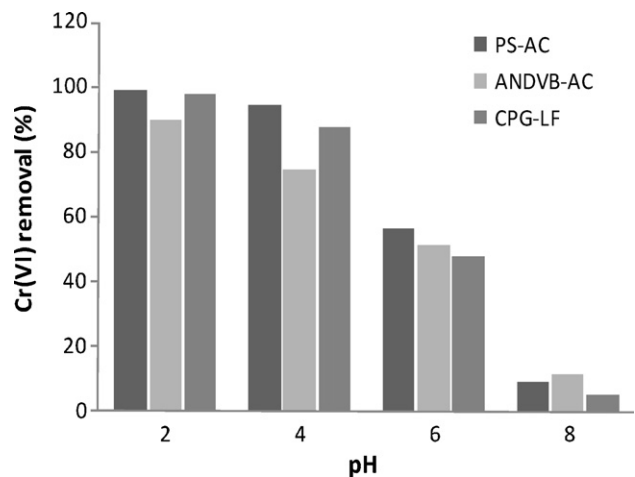


Fig. 8. Cr(VI) removal percentage of PS-AC, ANDVB-AC and CPG-LF at different pH.

4. Conclusions

Peach stones and macroporous acrylonitrile-divinylbenzene copolymer have been successfully converted to microporous activated carbons. Produced activated carbons have relatively high surface area and pore volume that can be compared with commercial CPG-LF carbon. SEM images demonstrate that while ANDVB-AC shows a spongy structure, the surface of PS-AC is like a honeycomb. Both carbon samples possess acidic oxygen functionalities, mainly in the form of phenolic groups. Air oxidation caused an

increase in oxygen containing functional groups, while pyridine type, nitrogen-containing groups could significantly contribute to the basicity of ANDVB-AC. According to the PZC values, the surface of produced carbons has been positively charged up to pH ~8. Prepared activated carbons showed high Cr(VI) adsorption capacity. Adsorption of Cr(VI) was greatly affected by solution pH and was superior at low pHs. Cr(VI) sorption capacity of peach stone based activated carbon was equal to that of commercial activated carbon and higher than that of polymer based carbon.

Electrostatic attraction between protonated carbon surface and hydrogen chromate anions is predominated for PS-AC and CPG-LF, but not for ANDVB-AC. There must be another process, which is more effective than electrostatic attraction in the case of ANDVB-AC, like complex formation between hydrogen chromate and pyridine groups, that could also be responsible for adsorption of Cr(VI) ions. The produced carbons could be evaluated as potential adsorbents to remove Cr(VI) from aqueous media effectively.

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