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Applied Surface Science xxx (2006) xxx–xxx

applied
surface science

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Synthesis and characterization of activated carbon from asphalt

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Received 22 December 2005; received in revised form 9 January 2006; accepted 10 January 2006

Abstract

Asphalt (cheap and available in huge amount in Jordan) was converted into activated carbon powder by chemical treatment with sulphuric and nitric acids at 450 °C. The final product was characterized and found effective as adsorbent material. Its cation exchange capacity reaches 191.2 meq/100-g carbons when treated with 30 wt% acid/asphalt ratio without airflow rate injection and 208 meq/100-g carbons when 6.5 ml air/min was injected into the surface of the asphalt during activation at the same acid/asphalt weight ratio of 30 and temperature 450 °C. The zero point of charge for this product was found to be stable at pH value around 3 in the range of initial pH between 3 and 10.

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PACS: 80

Keywords: Asphalt; Activated carbon; Chemical activation; Ion exchange

1. Introduction

Environmental pollution is currently one of the most important issues facing humanity. It has increased exponentially in the past few years and reached alarming properties in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Industrial wastewaters containing arsenic, lead, copper, cadmium, and chromium, for example, can contaminate groundwater resources, and thus lead to serious groundwater pollution problems. On the health side, exposure to such chemicals can damage the central nervous system, respiratory system, kidney, and blood system if entered human body. Therefore, removing these toxic heavy metals or decreasing their concentrations to the permitted levels before discharging becomes a challenging issue.

It is known that adsorption is one of the most efficient methods for the removal of colors, odor, oils, and organic pollutants from process or waste effluents. Although, activated carbon (granular or powdered) is the most widely used

adsorbent due to its excellent adsorption capability for organic pollutants as result of having relatively low molecular weight, its usage is often limited due to its high cost [1].

Almost any carbonaceous material from plants or minerals origin can be converted to activated carbon if properly treated. It has been prepared from animal's source and plant origin, such as coconut shells [2], almond shells [3], olive stones [4], corncobs [5], and apricot stones [6], all of them have been used with varying success for this purpose.

The surface chemistry of a commercial activated carbon has been selectively modified by Pereiras et al. [7] without changing significantly its textural properties, by means of chemical and thermal treatments. They found that the surface chemistry of the activated carbon plays a key role in dye adsorption performance. The basic sample obtained by thermal treatment under H₂ flow at 700 °C is found the best material for the adsorption of most of the dyes tested.

Chen et al. [8] used citric acid to modify a commercially available activated carbon to improve copper ion adsorption from aqueous solutions. The carbon was modified with 1.0 M citric acid, followed by an optional step of reaction with 1.0 M sodium hydroxide. It was found that the surface modification reduced the specific surface area by 34% and point of zero charge (pH_{pzc}) of the carbon by 0.5 units and increased the adsorption capacity to 14.92 mg Cu/g, which was 140% higher than the unmodified carbon. They also found that the

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67 modification did not change both external diffusion and
68 intraparticle diffusion.

69
70 Molina-sabio et al. [9] used phosphoric acid as activating
71 agent in the preparation of binder less activated carbon discs.
72 The granular precursor was impregnated with different
73 solutions of phosphoric acid, hot pressed in discs, heat treated
74 under a flow of nitrogen and washed with distilled water to
75 extract the excess acid. Best results (storage capacity of 131,
76 v/v) were obtained when using an impregnation ratio
77 $X_p = 0.35$ g phosphorous/g precursor and conforming at
78 100°C . Some discs were additionally activated under a flow
79 of carbon dioxide; the maximum methane storage capacity
80 (near 150, v/v) being obtained when burn-off is in the 10–40%
81 range.

82 García et al. [10] studied the influence of the surface
83 chemistry in the adsorption of Phenanthrene (Phe) vapour on
84 oxidized activated carbons using a fixed bed reactor with a
85 process temperature of 150°C , similar to the observed in the
86 flue gases from energy generation systems. They used a
87 commercial activated carbon as raw material. The oxidized
88 activated carbons were obtained by treatment with HNO_3 and
89 H_2O_2 at different concentrations. The new adsorbents were
90 prepared to have similar porosity but different surface
91 chemistry. They observed that the higher the total number of
92 oxygen surface groups, the lower the Phenanthrene adsorption
93 capacity.

94 Villacañas et al. [11] investigated the adsorption of model
95 aromatic compounds on commercial activated carbon that
96 modified by means of chemical and thermal treatment under a
97 flow of H_2 . They found that the textural properties were not
98 significantly changed after these modifications and the best
99 uptake for all the adsorptives under most of the pH conditions
100 used corresponded to the basic sample, which means that
101 dispersive interactions are the most important in this process.
102 However, they also reported that electrostatic interactions could
103 not be neglected.

104 Figueiredo et al. [12] used three natural waste materials
105 containing chitin as adsorbents for textile dyestuffs, namely
106 the Anodonta shell, the Sepia and the Squid pens. The
107 selected dyestuffs were the Cibacron green T3G-E, and the
108 Solophenyl green BLE 155%, both from CIBA, commonly
109 used in cellulosic fibres dyeing, the most used fibres in the
110 textile industry. They found that the materials' adsorption
111 capacities increase after a simple and inexpensive chemical
112 treatment, which increases their porosity and chitin relative
113 content

114 There are some literatures related to synthesis of activated
115 carbon from petroleum residues. However, this work is being
116 conducted to evaluate the possibility of the use of asphalt as a
117 raw material for pollution control. The asphalt used in this work
118 is obtained from Jordanian Petroleum Refinery Ltd., which
119 produces about 1400 tonnes of asphalt daily. This amount
120 consists 10% of the total refined petroleum, which is used in the
121 roads and constructions as it has low selling price (US\$ 80 per
122 tonne). Therefore, the production of efficient activated carbon
123 from asphalt to be used as an adsorbent for removal of
124 pollutants will be economically feasible.

2. Experimental procedure

2.1. Preparation of activated carbon

126
127 Asphalt was used in this work as a raw material to produce
128 activated carbon. This material was mixed with concentrated
129 sulphuric acid to obtain mixtures with different weight ratios of
130 acid/asphalt ranging from 20:1 to 60:1. These mixtures were
131 agitated vigorously at temperature values ranging from 450 to
132 900°C , while compressed air was sparged through out the
133 solution as shown in Fig. 1. Small amount of concentrated nitric
134 acid (from 3 to 10 ml) was added to the mixture in order to
135 enhance the oxidation of the produced activated carbon. When
136 the reaction was completed, the remaining solid was washed
137 with distilled water several times to reach a pH value about 4,
138 then few drops of diluted NaOH (0.1 M) was added to raise the
139 pH to 7. Then the mixture was dried at 105°C for 1 h to remove
140 any remaining water, and stored in close tight containers for
141 analysis and uses.

2.2. Characterization of the produced activated carbon

142
143 All the produced activated carbon samples were character-
144 ized by their physical and chemical properties according to the
145 American Society for Testing Materials (ASTM). These
146 properties are listed in Table 1.

2.2.1. Apparent density

147
148 Ten grams of the produced activated carbon was taken as dry
149 basis, one-third of this sample was transferred to 100-ml
150 graduated cylinder, and tamping with a rubber pad. Activated
151 carbon was being added until the entire original sample (10 g)
152 was transferred to the cylinder. Tamping was continued for 5 min
153 until there was no further settling produced. The volume was
154 recorded and the apparent density was calculated on the dry basis:

$$\text{apparent density} = \frac{\text{weight of the sample (g)}}{\text{volume of the sample (l)}} \quad (1)$$

2.2.2. Iodine number

157
158 The iodine number is defined as the milligrams of iodine
159 adsorbed by 1 g of activated carbon. It is used to measure the
160 porosity of the activated carbon by adsorption of iodine from
161 solution. Each 1.0 mg of iodine adsorbed is considered to
162 represent 1.0 m^2 of activated carbon internal surface area [5].

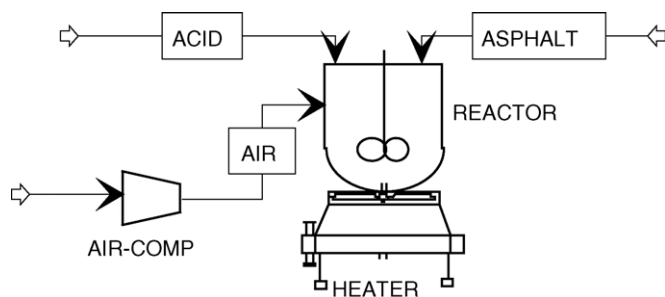


Fig. 1. Experimental setup for converting asphalt into activated carbon.

Table 1
Typical properties of the produced carbon and the CAC

Property	ASTM method	Produced carbon	CAC
Ash content (wt%)	D2866-94(2004)	4.9	6
Density (g/dm ³)	D2854-96(2004)	189	340
pH	D3838-80(1999)	Acidic	Alkaline
Moisture (wt%)	D2867-99	10.3	10
Iodine number	D4607-94(1999)	2217	650

Table 2
Effect of acid type on activation time

Activation time (min)	Type of acid
180	Acetic acid
210	Phosphoric acid
40–60	Sulphuric acid
Instantaneously	Nitric acid

2.2.3. Ash content

One gram of the produced dried activated carbon was transferred into a clean dry crucible. The crucible with its content was weighed, then the crucible was placed in a furnace and the temperature was raised to 973 K. After 4 h, the crucible was cooled to room temperature and weighed. Then the ash content was calculated:

$$\text{ash content (\%)} = \frac{\text{weight of the ash (g)}}{\text{weight of the original sample (g)}} \times 100\% \quad (2)$$

2.2.4. Cation exchange capacity

Sample of 4 g of the produced carbon was mixed with 33 ml of 1 M sodium acetate solutions, resulting in an exchange between the added sodium ions and the matrix cations. Subsequently, the sample was washed with 33 ml of isopropyl alcohol. A volume of 33 ml ammonium acetate solution (1 M) was then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium was then determined by SOLAAR S4 atomic absorption spectrophotometer.

2.2.5. Zero point of charge

Batch equilibrium technique was applied to determine the pH at the zero point of charge. Portions of the produced activated carbon powder (0.5 g) were introduced into a known volume (20 ml) of 0.1 M KNO₃ solution. Potassium nitrate (KNO₃) was selected as an inert electrolyte.

Initial pH values (pH_{initial}) of KNO₃ solutions were adjusted to cover the range from 4.5 to 11.5 by adding 0.1 M HNO₃ or KOH. The solutions were allowed to equilibrate for 24 h in an isothermal shaker at 25 ± 1 °C. Then the suspensions were filtered through filter paper and the pH values (pH_{final}) were measured again using ion-pH meter [13].

3. Results and discussions

Table 1 lists the measured characteristics of the produced activated carbon obtained using ASTM tests, and those of the commercial activated carbon (CAC) produced by Norit Chemical Company. The produced carbon from asphalt shown lower ash content and density compared with those of Norit. The iodine number of the produced carbon is high at 2217 which is 3.4 times higher than that of Norit, indicating that the produced carbon is an activated carbon with a high surface area. On the other hand, the produced carbon has an acid nature as a result of activation with sulphuric and nitric acids.

3.1. Effects of activation conditions

Table 2 shows the time needed to produce activated carbon from asphalt for different types of acids when acid/asphalt weight ratio was 30 and the temperature 300–450 °C. It is cleared that 180 min is required to activate the asphalt using acetic acid; 210 min using phosphoric acid while 40–60 min are enough in the case of sulphuric acid. The differences in the activation times are attributed to the differences in the strength of acids used (nitric acid > sulphuric acid > acetic acid > phosphoric acid). Addition of nitric acid showed an instantaneous reaction with the asphalt where NO_x was evolved out of the mixture. No yield of activated carbon was noticed by using this acid. Therefore, sulphuric acid with trace amount of nitric acid was chosen as an activation agent.

Fig. 2 illustrates the effect of acid/asphalt mass ratio on the yield of the produced activated carbon. It is clear that the yield of the produced activated carbon decreases with increasing acid/asphalt weight ratio. It is also noticed that the increasing of this ratio will increase the time required to complete the activation (Fig. 3). Therefore, a good link may be attributed to the fact that more volatile compounds could evaporate out of the mixture before conversion. The increase in this ratio also has a noticeable effect on the cation exchange capacity (CEC) of the produced carbon as shown in Fig. 4. It is apparent that the CEC increases with increasing

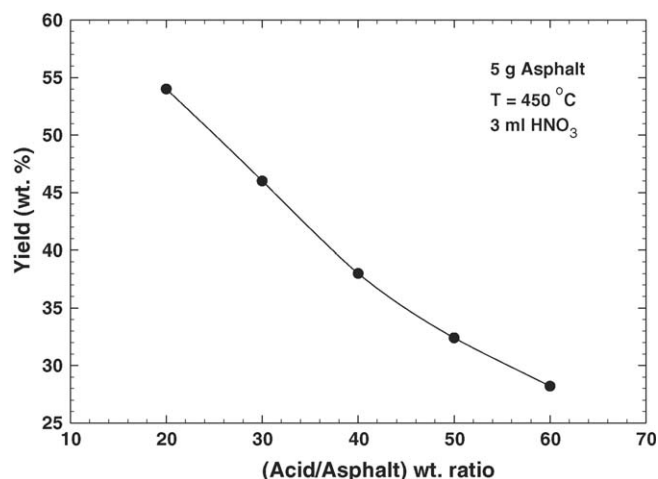


Fig. 2. Effect of acid/asphalt mass ratio on the yield of produced activated carbon.

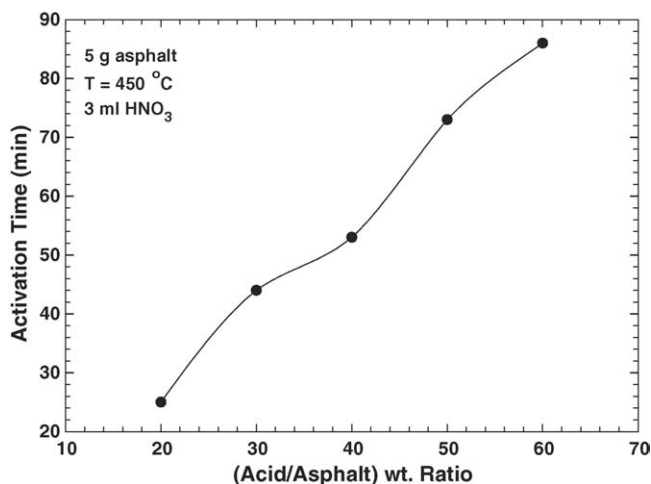


Fig. 3. Acid/asphalt weight ratio effect on the activation time.

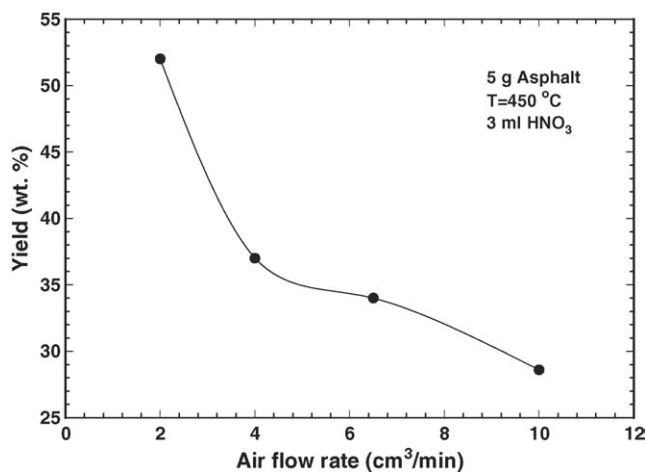


Fig. 5. Effect of airflow rate on the yield of the produced activated carbon.

230 acid/asphalt ratio from 20 to 30 then start to decrease. A
 231 maximum value of CEC of 191.2 meq/100 g-carbon was
 232 obtained when the mass of acid was 30 times that of asphalt.
 233 On the other hand, the decrease in the CEC after this ratio
 234 (from 191.2 to 154.5 meq/100 g-carbon) is due to the
 235 destruction in the carbon structure and the blockage of the
 236 micropores and mesopores by fine carbon particles resulted
 237 from highly oxidation with acid.

238
 239 Effect of sparged airflow rate during activation on the yield
 240 of the activated carbon is illustrated in Fig. 5. It is shown that
 241 the yield of the produced activated carbon decreased from
 242 2.64 to 1.4 g when sparged air increased from 1.8 to 10.7 ml/
 243 min. This is attributed to the increase in the degree of burning
 244 of the produced carbon at elevated temperature, which
 245 decreases the amount of the produced carbon per batch. On
 246 the other hand, the increase in the airflow rate increased the
 247 cation exchange capacity as shown in Fig. 6. This is due to the
 248 enhancement in the oxidation of carbon atoms and increasing
 249 the formation of the functional groups on the surface of the
 250 activated carbon. When airflow rate further increases to a

value greater than 6.25 ml/min, the CEC start decreasing and
 251 the efficiency of the produced activated carbon get lowered.
 252 This finding could be ascribed to the decrease in heat of
 253 reaction during activation that resulted from excess airflow
 254 rate on the carbon surface. This is cleared in Fig. 7, where the
 255 increase in reaction temperature from 300 to 900 °C increased
 256 the CEC from 164.5 to 224.6 meq/100 g-carbon. On the
 257 contrary, the yield of the carbon decreased from 2 to 1.54 g
 258 based on 5 g initial weight (Fig. 8). This is expected as some
 259 parts of the carbon and volatile compounds may escape with
 260 the exhaust gases as a result of burning during activation. The
 261 optimum temperature of activated solution could be figured
 262 out to be 450 °C. Above this value the production process
 263 becomes economically infeasible due to the higher energy
 264 demand for small increase in the CEC value. Nevertheless, the
 265 time required to activate the carbon is high at low activation
 266 temperature. A maximum period of 60 min was reached when
 267 the activation temperature was 300 °C. Then the required time
 268 decreased sharply to about 40 min when the temperature
 269 reaches 450 °C as cleared in Fig. 9. Between temperatures
 270

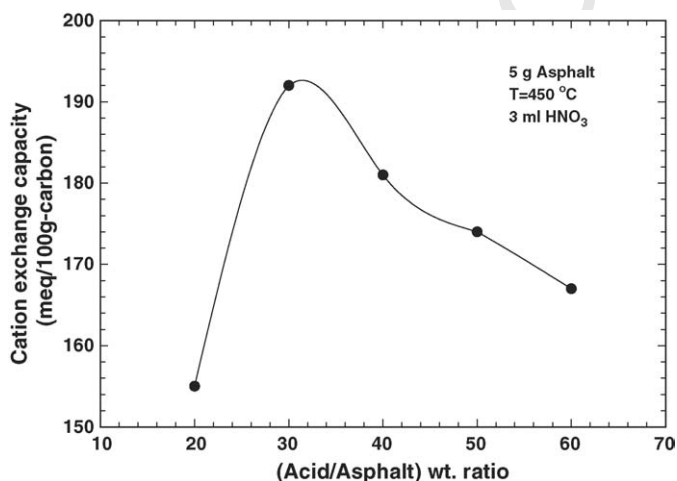


Fig. 4. Cation exchange capacity of the produced carbon from asphalt.

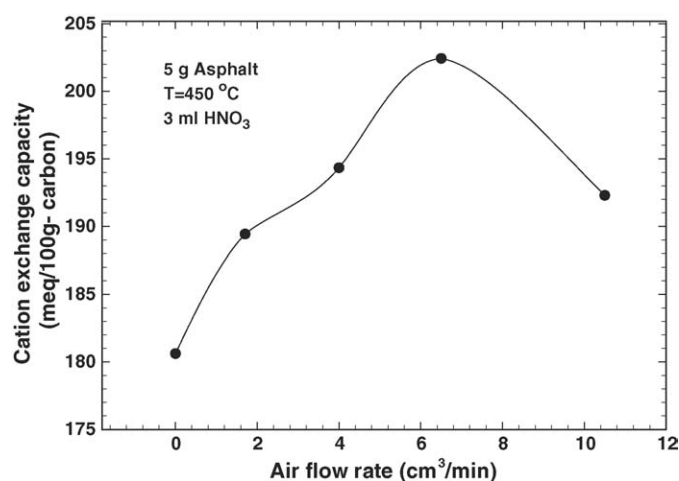


Fig. 6. Effect of airflow rate on the cation exchange capacity of the carbon.

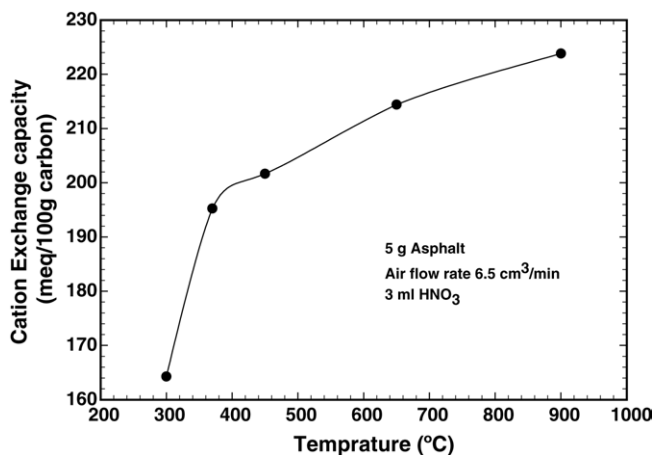


Fig. 7. Effect of solution temperature on cation exchange capacity of the carbon.

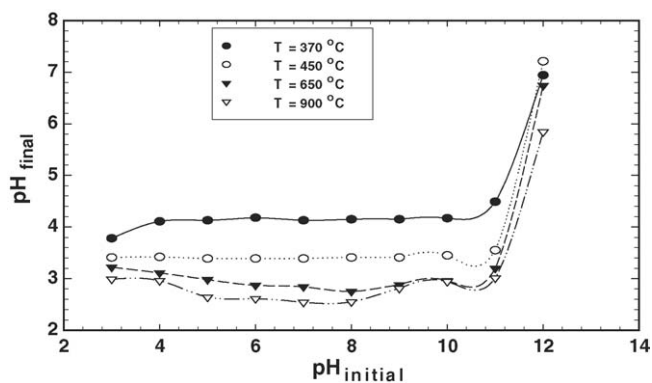


Fig. 10. Temperature effect on the zero point of charge.

270
271
272

450 and 900 °C, the decrease in the activation time was low (i.e., from 40 to 28, respectively).

3.2. Zero point of charge

Characterization of the produced activated carbon surface is governed by its ability for adsorption of target solute. One of the major factors that control sorption uptake is the distribution of charge on the adsorbent surface. The surface of adsorbent, in general, either has positive or negative charge. This distribution of charge resulted from the interaction of surface with solute ions. In another words, there will be a point or a state at which the surface has zero point of charge (ZPC) where the adsorption takes place by diffusion into the micropores and mesopores. If the pH of the solution is high enough, the surface becomes negatively charged and the positive ions will be attracted on the surface according to electrostatic attraction, while the negative ions will be attracted at pH below the ZPC.

Fig. 10 shows the effect of temperature on the zero point of charge for the produced activated carbon. Increasing the

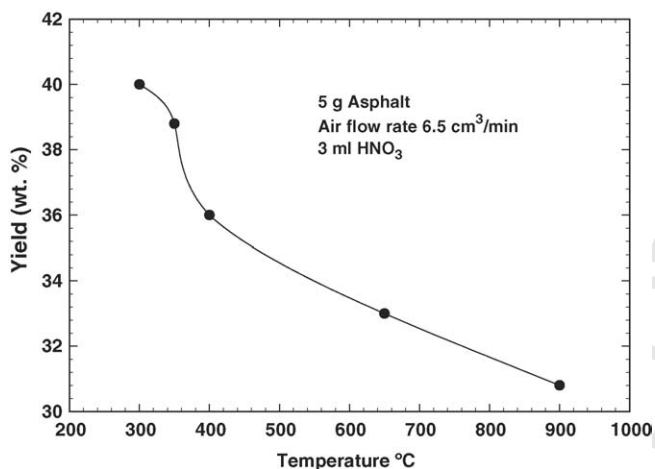


Fig. 8. Effect of temperature on the yield of produced carbon.

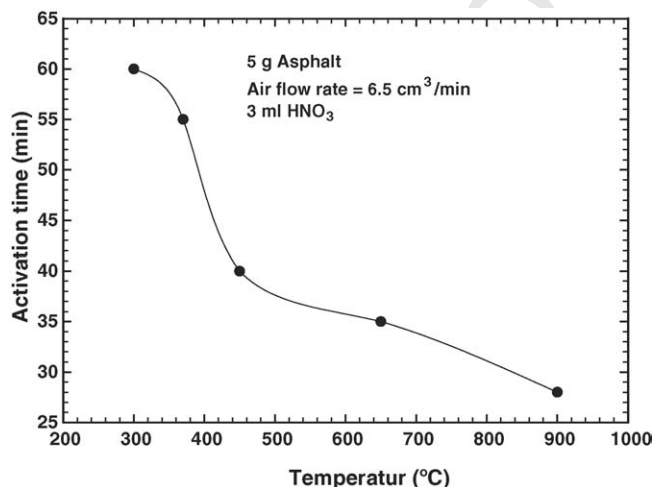


Fig. 9. Temperature effect on the activation time required to produce the activated carbon.

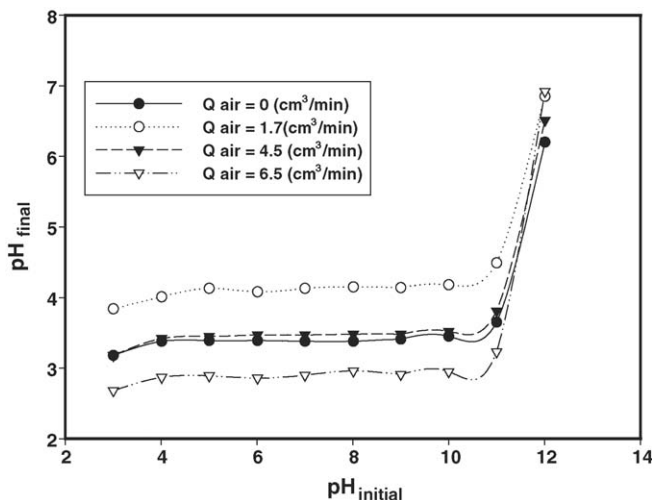


Fig. 11. Airflow rate effect on the zero point of charge.

280 activation temperature from 370 to 900 °C decreasing the
291 pH_{ZPC} from 4.2 to 2.89. This can be explained by the fact that
292 increasing the activation temperature increases the functional
293 groups on the surface of the activated carbon. The stability of
294 final pH of solution at this wide range of initial pH from 3 to 10
295 supports the use of this type of activated carbon as good
296 adsorbent.

297 Fig. 11 shows that increasing the sparged airflow rate
298 resulted in an increase in the rate of oxidation of the carbon
299 atoms through the reaction, which increases the functional
300 groups on the surface of activated carbon that is mainly
301 carboxylic group with negative charge.

4. Conclusions

302
303 The conversion of asphalt into activated carbon powder
304 with high cation exchange capacity and low zero point of
305 charge obtained at wide stable initial pH range from 3 to 10
306 was successfully achieved. The yield of the produced
307 activated carbon was affected with increasing acid/asphalt
308 weight ratio and/or airflow rate. The maximum value of CEC
309 was obtained at 30 acid/asphalt weight ratio. This CEC was
310 found to increase with the increasing airflow rate and
311 temperature. The zero point of charge was found to decrease
312 with the increase in the activation temperature and airflow
313 rate.

Acknowledgments

The authors gratefully acknowledge the financial support of
Jordan University of Science & Technology to this work and
Mutah University for carrying out part of the experimental and
analytical works in its laboratories.

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