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Short communication

Production of granular activated carbon from waste *Rosa canina* sp. seeds and its adsorption characteristics for dye

A. Gürses [a,*], Ç. Doğar [b], S. Karaca [c], M. Açikyildiz [a], R. Bayrak [a]

[a] *Department of Chemistry, Atatürk University, K.K. Eğitim Fakültesi, 25240 Erzurum, Turkey*
[b] *Department of Science Education, Atatürk University, Erzincan Eğitim Fakültesi, 24030 Erzincan, Turkey*
[c] *Department of Chemistry, Atatürk University, Fen-Edebiyat Fakültesi, 25240 Erzurum, Turkey*

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Abstract

An activated carbon was developed from *Rosa canina* sp. seeds, characterized and used for the removal of methylene blue (basic dye) from aqueous solutions. Adsorption studies were carried out at 20 °C and various initial dye concentrations (20, 40, 60, 80, and 100 mg/L) for different times (15, 30, 60, and 120 min). The adsorption isotherm was obtained from data. The results indicate that the adsorption isotherm of methylene blue is typically S-shaped. The shape of isotherm is believed to reflect three distinct modes of adsorption. In region 1, the adsorption of methylene blue is carried out mainly by ion exchange. In region 2 by polarizations of π-electrons established at cyclic parts of the previously adsorbed methylene blue molecules is occurred. However, it is not observed any change at the sign of the surface charge although zeta potential value is decreased with increase of amount adsorbed. In region 3, the slope of the isotherm is reduced, because adsorption now must overcome electrostatic repulsion between oncoming ions and the similarly charged solid. Adsorption in this fashion is usually complete when the surface is covered with a monolayer of methylene blue. To reveal the adsorptive characteristics of the produced active carbon, porosity and BET surface area measurements were made. Structural analysis was performed using SEM–EDS. The produced active carbon has the specific surface area of 799.2 $m^2\ g^{-1}$ and the iodine number of 495 mg/g.

Keywords: *Rosa canina*; Iodine number; Adsorption isotherm; Chemical activation; Active carbon

1. Introduction

There is a considerable need for the removal of color from wastewater/effluents. The discharge of dye-bearing wastewater into natural streams and rivers from the textile, paper, carpet, leather, distillery, and printing industries poses severe problems. Various methods of dye/color removal, including aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation, electrochemical treatment, dilution, filtration, flotation, softening, hydrogen peroxide catalysis, and reverse osmosis, have been proposed from time to time. However, all of these methods suffer from one or another limitation, and none of them were successful in completely removing the color from wastewater [1–4].

Adsorption now plays a key role in modern industries, especially in the field of environmental protection engineering, with the increasing environmental awareness of people all over the world. Adsorption processes are being employed widely for large-scale biochemical, chemical and environmental recovery and purification applications. Liquid–solid adsorption operations are concerned with the ability of certain solids to preferentially concentrate specific substances from solution onto their surfaces, such as the removal of moisture dissolved in gasoline, the decolorization of petroleum products, and the removal of pollutants from aqueous or gaseous effluents [5].

Activated carbons are of interest in many economic sectors and concern many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing. Physicochemical characteristics of activated carbon depend on the kind of raw material used and activation conditions. Activated carbons are classified into one of three types, such as powder, granular, and fibrous according to its size and shape, and each type has its specific application.

* Corresponding author. Tel.: +90 442 231 4004; fax: +90 442 236 0955.
E-mail address: ahmetgu@yahoo.com (A. Gürses).

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Raw materials for activated carbon are chosen depending on their purity, price, potential extent of activation, and stability of supply. They derive their adsorptive properties from the extensive internal pore structure that presents a high surface area available for the adsorption of molecular species. Such high porosity is a function of both the precursor as well as the scheme of activation. Precursors to activated carbons are either of botanical origin (e.g. wood, coconut shells and nut shells) or of degraded and coalified plant matter (e.g. peat, lignite and all ranks of coal). Agricultural wastes are considered as very important feedstocks in virtue of two facts: they are renewable sources and low cost materials. In recent years, condensed research on activated carbons from agricultural residues has been reported, e.g. apricot stones, peach stones, cherry stones, date pits, wheat straw, pecan shells, hulls of soybean and rice, walnut shells and many others (grape seeds, plum stones, almond shells). Very little has been mentioned about corncobs although this is a cheap and abundant agricultural waste of no economical value [6–8].

Chemical activation involves impregnation of the raw material with chemicals such as phosphoric acid, potassium hydroxide, and zinc chloride. Although, phosphoric acid is shown to be the most environmentally sound chemical for the activation processes, most studies have used zinc chloride due to its effective activating capability. The common feature of these impregnates is their ability for carbonization and therefore, development of a desired pore structure. The degradation of cellulose material and the aromatization of the carbon skeleton upon $ZnCl_2$ treatment result in the creation of the porous structure. The scientific literature contains some interesting papers on $ZnCl_2$ activation of different lignocellulosic wastes like almond shells, peach stones, olive stones and holm oak sawdust [9]. Zinc chloride acts as a dehydrating agent that promotes the decomposition of carbonaceous material during the pyrolysis process, restricts the formation of tar, and increases the carbon yield. Essentially, vacant interstices in the carbon matrix are formed upon extensive post-pyrolysis washing of the pores. The extent of chemical activation can significantly alter the characteristics of the produced carbons. This process results in the enhancement of the meso- and macropore formation [10,8]. The chemical activation process is known to be effective for the production of activated carbon used for water/wastewater treatment. Among the chemical activating agents, zinc chloride in particular is the most widely used chemical in the preparation of activated carbon [11].

The adsorption of methylene blue from the aqueous phase is a useful tool for product control of sorbents. It is for this reason that, in order to characterize the adsorption capacity of a material, determining its surface area and pore size distribution would not be enough; sorbents having the same surface areas often exhibit different adsorptive behavior. Methylene blue (MB) is among the cationic adsorbates most often used in such studies [4].

In this study, *Rosa canina* sp. seeds wastes were utilized as the raw material for the production of granular activated carbon by chemical activation and its adsorption capacity for methylene blue, which is a cationic dye, was evaluated. The activating agent used was zinc chloride and weight ratio of raw material was 1:5. The specific surface area and the total pore volume of produced activated carbon were determined by using BET-N_2 method and Hg porosimeter. Adsorption time and initial concentration of methylene blue were considered as variables for the adsorption experiments.

2. Materials and methods

2.1. Materials and apparatus

Rosa canina sp. seeds were used as the raw material from Gümüşsu Herbal Tea Plant wastes, Gümüşhane, in Turkey. Chemical analysis results of raw material [12] are given in Table 1.

Pyrolysis experiments were carried out in a fixed bed reactor as shown schematically in Fig. 1. The system consists of a porcelain furnace conducted in a packed column, sample holder, a temperature control unit and some necessary facilities. Sample

Table 1
Chemical composition of *Rosa canina* fruits

Chemicals	
Vitamin C (mg/100 g)	624
Ash (%)	3.40
Total dry matter (%)	34.3
Total sugar (%)	16.2
Reducing sugar (%)	15.1
Cellulose (%)	11.15
Water (%)	65.7
Protein (%)	3.17
Total acid pH	4.01
Minerals	
P (mg)	123
K (mg)	390
Ca (mg)	11.0
Mg (mg)	15
Fe (mg)	2.0
Cu (mg)	0.19
Zn (mg)	0.30
Mn (mg)	0.17
Na (mg)	1.7

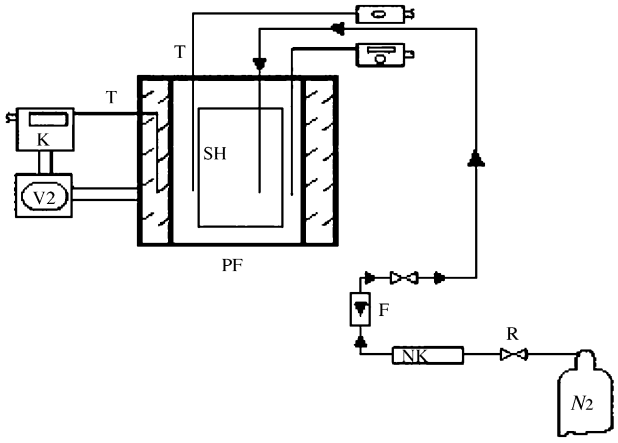


Fig. 1. Schematic diagram of the apparatus used in pyrolysis experiments. PF: programmable furnace, K: controlling system, O: recorder, SH: sample holder, T: thermocouple, F: flow meter, NK: driver, R: pressure regulator, V: valf, V2: transformer.

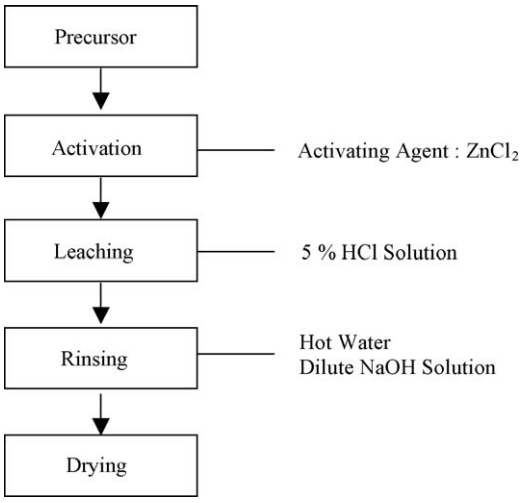
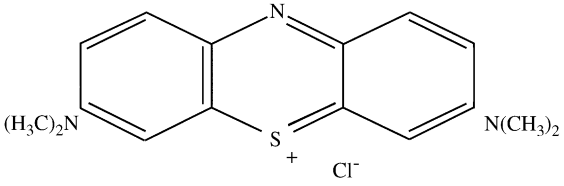


Fig. 2. Flow diagram for activation process.

holder, made of stainless steel with 3.0 cm inner diameter and 14.0 cm length having a sample room was placed into middle of porcelain furnace, which was heated by an electrical power. The temperature was measured and controlled in the middle of the porcelain furnace and in the raw sample by a two Ni–Cr thermocouple. The furnace is safely held at desired temperature by this controlling system. To maintain inert atmosphere, highly pure N_2 gas (>99.999%) was charged to the furnace at the flow rate of 2100 mL min^{-1} during the activation process.

All chemicals used in this study were obtained from Merck. As adsorbate, a cationic dye, methylene blue (MB), was chosen. MB is a basic blue dyestuff, CI Classification Number 52015, its formula is $C_{16}H_{18}N_3SCl$ and its structure is as follows:



BET surface area and porosity measurements of produced active carbon sample were made by Micromeritics FlowSorb II-2300 and Autopore II 9220 Hg porosimeter (maximum Hg pressure 40,000 psi), respectively. Structural analysis was performed using SEM–EDS. The concentration of methylene blue in the supernatant solution after and before adsorption was determined using a double-beam UV spectrophotometer (Schimadzu) at 666 nm.

2.1.1. Activation

The general procedure of the activation process for this study is described by Kim et al. [7] with a few modifications as below and is schematically outlined in Fig. 2.

1. A mixture of *Rosa canina* sp. seeds and 3 M $ZnCl_2$ (Merck) solution was put in a sample reactor and heated in the furnace at a controlled temperature for an hour.
2. Thermally treated product was boiled in 5% HCl solution to leach out the activating agent; it was rinsed with hot distilled water several times. Then, it was rinsed again with dilute NaOH solution for neutralization.
3. The samples were then vacuum-dried at 102 °C. A final product yield or loss due to washing was recorded.
4. The final product was stored in a desiccators filled with N_2 gas to prevent oxidation.

The ultimate analysis results for produced activate carbon are given in Table 2.

The activated carbons were weighed to determine activation burn-off or mass loss due to activation and calculated the following equation [13]:

$$\text{activation burn-off}\,(\%) = 100 - \left\{\left[\frac{\text{mass after activation (g)}}{\text{original mass (g)}}\right] \times 100\right\} \quad (1)$$

Activation treatments were performed at activation temperatures of 350, 500, 600, and 700 °C and the weight ratio of raw material and $ZnCl_2$ solution of 1:5. The surface areas of the carbonized samples at 350, 500, 600, and 700 °C were found to be 271.7, 799.5, 685.7, and 633.2 $m^2\ g^{-1}$, respectively. Also, the porosity values and the adsorption uptakes of these samples were measured as 28.7%, 43.5%, 46.2%, and 43.0%, and 47.0, 47.2, 47.2, and 45.9 mg/g, respectively. Therefore, the temperature of 500 °C was chosen as optimum carbonization temperature.

2.2. Characterization of activated carbon

2.2.1. Adsorption test

Adsorption experiments were carried out by agitating 0.2 g of adsorbent with 100 mL of dye solution of desired concentration at pH 6.5 at room temperature (20 ± 1 °C) in a rotary shaker at 90 rpm. The samples were withdrawn from the shaker at pre-determined time intervals, and the dye solution was separated from the adsorbent and centrifuged at 3500 rpm for 5 min. The absorbance of the supernatant solution was then measured. Calibration experiments were carried out to exclude the experimental mistake raised from sorption of MB on wall of the glass vessels. The amount of adsorbed at time t, Y (g/g), was calculated by

$$Y = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_t are the liquid-phase concentrations initially and at time t, respectively (g/mL), V is the volume of solution (mL), and W is the weight of dry adsorbent (g).

Table 2
Elemental analysis of produced activated carbon

Elemental analysis	wt.%
C	71.25
H	3.07
N	1.86
S	0.33
O (by diff.)	23.49

Table 3
Some characteristics of produced activated carbons

Carbonization temperature (°C)	500
Specific surface area (BET-N_2) ($m^2\ g^{-1}$)	799.52 ± 0.06
Porosity (%)[a]	43.50
Bulk density ($g\ mL^{-1}$)[a]	0.47
pH	4.23
Average pore diameter (nm)	5.21
Burn-off (%)	64.00
Zeta potential of raw material (mV)	−32.8
Zeta potential after adsorption (mV)[a]	−6.0
Iodine number (mg/g)	495.0
Moisture (%)	12.4

Adsorption time: 1 h, initial methylene blue concentration: 100 mg/L, adsorption temperature: 293 K.
[a] These are values for the powder active carbon sample passed from 100 mesh sieve.

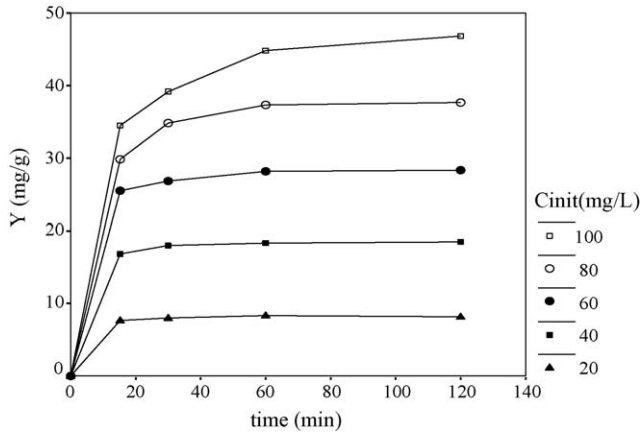


Fig. 3. The variation of the amount adsorbed with adsorption time at 20 °C.

2.2.2. Iodine number

The iodine number (q_{iodine}) of activated carbon was obtained at 20 ± 1 °C on the basis of the Standard Test Method, ASTM Designation D4607-86 [14]. The activated carbons (1, 2 and 3 g) were placed respectively in a dry 250-cm^3 Erlenmeyer flask equipped with a ground glass stopper, and was fully wetted with 10 cm^3 of 5 wt.% HCl. One 100 mL of 0.1 mol/L iodine solution was poured into the flask, and the contents were vigorously shaken for 30 s. After rapid filtration, 50 mL of the solution was titrated with 0.01 M sodium thiosulfate until the solution became pale yellow. Then, 2 mL of starch indicator solution (1 g/L) was added and the titration was continued with sodium thiosulfate until the solution became colorless. The concentration of iodine in the solution was thus calculated from the total volume of sodium thiosulfate used and the volume dilution factor. The iodine number of produced active carbon is given in Table 3.

2.2.3. Zeta potential measurements

Zeta potentials of solid particles in activated carbon/water suspensions at natural pH were measured by using Zeta Meter 3.0+.

3. Results and discussion

3.1. The adsorption of methylene blue

The results for variation of amount adsorbed of methylene blue at 20 °C with contact time (15, 30, 60, 120 min) are given as a function of initial concentration (from 20 to 100 mg/L) of methylene blue in Fig. 3. As seen from Fig. 3, to reach the adsorption equilibrium is sufficient 15 min at low and middle dye concentrations while 1 h for high dye concentrations. The rapid adsorption occurring at relatively low dye concentrations indicates the electrostatic attractive interaction acting between the activated carbon particles and methylene blue ions. The increase of the adsorption equilibrium with increasing of dye concentration could be attributed that the presence of the heteroporous structure of the activated carbon, which are mostly micropores and mesopores, and are firstly filled into micropores and then into meso- and macropores. As an alternative, Hu et al. [15] reported that the use of $ZnCl_2$ as activating agent not only creates more new pores, but also widens the pores. Therefore, considering formation of the pore geometries look-alike the ink bottle shape, the narrow parts of the activated carbons are firstly filled by methylene blue molecules. Adsorbed dye molecules lead sterically to hindering the usage of the micropores and so the reaching time to adsorption equilibrium rises.

Zinc chloride used as the activating agent lowers the carbonization temperature and brings about dehydration and oxidation of *Rosa canina* sp. seeds in the course of thermal treatment, resulting in the development of microporous structure of activated carbon. Well-developed micropores can provide the adsorbent with a high specific surface area and adsorbability. The fact that a low relatively iodine value of 495 mg/g may be due to the thermal degradation of the formed activated carbon in this temperature (500 °C), which hinders its adsorption capacity so that the iodine value is decreased. In general, carbonization and activation temperature are known to be very influential on the micropore structures of activated carbon, which determines the adsorption capacity [7]. Also, carbons with higher burn-off percentage show higher adsorption capacity (in Table 3). This is due to the fact that more volatile compounds are released from the *Rosa canina* sp. seeds at higher burn-off treatment, which leads in turn to opening up the carbon structure and gives rise to more surface area.

The adsorption isotherm of methylene blue from aqueous solutions onto the produced active carbon at 20 °C is given in Fig. 4. From this figure, the adsorption isotherm is typically S-shaped. The shape of isotherm is believed to reflect three distinct modes of adsorption. In region 1, the adsorption of methylene blue is carried out mainly by ion exchange. In region 2 by polarizations of π-electrons at cyclic parts of the previously adsorbed methylene blue molecules is occurred. However, it is not observed any change at the sign of the surface charge although zeta potential value is low (see Table 3). In region 3, the slope of the isotherm is reduced, because adsorption now must overcome electrostatic repulsion between oncoming ions and the similarly charged solid. Adsorption in this fashion is usually completed when the surface is covered with a monolayer of methylene blue.

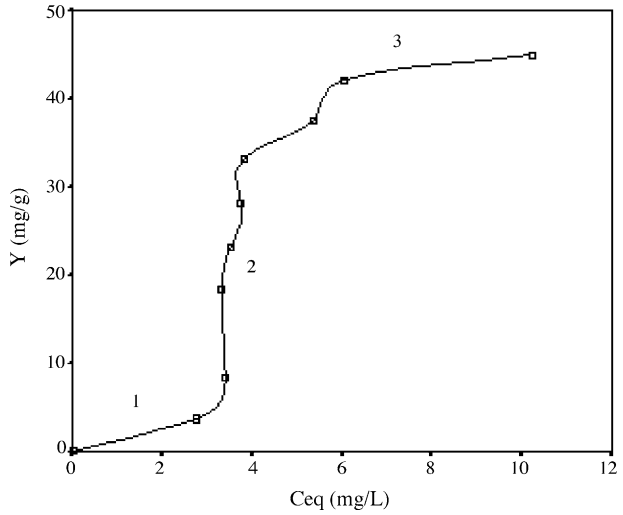


Fig. 4. Isotherm for adsorption of methylene blue onto the active carbon at 20 °C.

The size distribution of micropores of activated carbon is understood to be one of the critical factors determining its applicability [16]. The microstructures of the carbon were observed by SEM–EDS (Philips XL30S-FEG) and are shown in Fig. 5. This figure shows that the adsorbent had an irregular and highly porous surface, indicating relatively high surface areas. This observation is supported by the BET surface area of the activated carbon. The porosity of the carbon was around 43.50%. The porosity characteristics as well as the chemical nature of the activated carbons, play an important role in adsorption processes. The cellulose chars show that the produced active carbon has approximately equal macropores and micropores volumes. It is supposed that the predominantly mesopores and macropores structures of activated carbons from the *Rosa canina* seeds is due to the higher content of cellulose of 11.5% in the raw material. So, these data reveal the possibility of selecting the raw materials in accordance with the requirements of the porous structure of produced active carbons. Hence, if an activated carbon with a higher macropore volume is desired it will be necessary to use raw materials with a prevailing content of lignin and vice versa, in order to prepare carbons with predominantly micropores structure one should use raw materials with higher cellulose content [17,18].

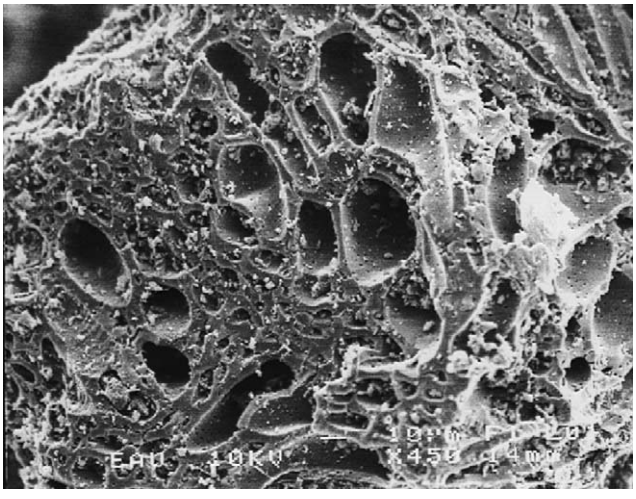


Fig. 5. SEM image of GAC at 500 °C.

Table 4
Produced activated carbons used as adsorbents for methylene blue

Adsorbent	Capacity (mg/g)	Reference
Activated olive stones with 40-wt.% $ZnCl_2$ at 600 °C	16.1	[19]
Activated olive stones with 40-wt.% $ZnCl_2$ at 600 °C in N_2 atmosphere	22.1	[19]
Activated furniture (850 °C)	200.0	[20]
Activated sewage char (800 °C)	120.0	[20]
Activated tyres (850 °C)	130.0	[20]
Pyrolysed furniture	80.0	[20]
Activated carbon from hazelnut shell at 750 °C	8.82	[21]
Activated carbon from walnut shell at 750 °C	3.53	[21]
Activated carbon from apricot stone at 750 °C	4.11	[21]
Activated carbon from almond shell at 750 °C	1.33	[21]
Activated tyre char	227.0	[22]
Activated *Rosa canina* seeds (500 °C)	47.2	Present work
Activated date pits (500 °C)	12.9	[23]
Activated date pits (900 °C)	17.3	[23]

The maximum adsorption capacities of methylene blue for the adsorbent used in this study along with that of other adsorbents are presented in Table 4. Although the adsorption capacity of produced activated carbon for methylene blue was normal, it was much higher than that of other potential adsorbents such as activated olive stones, activated carbon from hazelnut shell, activated carbon from walnut shell activated carbon from apricot stone, activated carbon from almond shell, and activated date pits. According to the results obtained, the produced activated carbon could be employed as low-cost adsorbent and could be considered as an alternative to commercial activated carbon for the removal of color.

4. Conclusion

Activated carbon prepared from *Rosa canina* sp. seeds, an agricultural waste, could be used as potential adsorbent for the removal of methylene blue from aqueous solutions. Batch experiments were conducted to assess the effect of concentration on GAC. The results indicated that adsorption process is usually complete when the surface is covered with a monolayer of methylene blue. Cost analysis for the preparation of activated carbon was not carried out, but as *Rosa canina* is found in abundance in Turkey, carbon cost is expected to be economical.

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