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# Comparison of Activated Carbon and Pyrolyzed Biomass for Removal of Humic Acid From Aqueous Solution

Cemal Emre Gokce, Sinan Guneysu*, Serdar Aydin and Semiha Arayici

*Department of Environmental Engineering, Faculty of Engineering, Istanbul University, 34320, Istanbul, Turkey*

**Abstract:** The pyrolysis of sewage sludge (SS) and olive mill waste (OMW) was carried out under nitrogen atmosphere and analyzed thermogravimetric and scanning electron microscopy micrographs. Removal capacity of pyrolyzed cokes was measured by humic acid solution. Humic substances can react with chlorine to produce carcinogens in drinking water. Activated carbon can be used as an effective treatment method to remove humic substances from water to prior to disinfection by chlorination. Olive mill waste, an agricultural byproduct and sewage sludge were used to produce activated carbon by pyrolysis with the addition of zinc chloride to enhance the reaction. Activated carbon was also produced using olive mill waste and sewage sludge. Both of them were compared to a commercially-available activated carbon product. Optimum pyrolysis conditions and concentration of the activating agent were identified. The equilibrium parameter model of the Freundlich isotherm and Langmuir isotherm was applied to the adsorption data, and the efficiency of pyrolyzed coke was determined. Activated carbon produced from olive waste material had a lower specific surface area (437.92 $m^2$/g) than activated carbon produced from sewage sludge (814.48 $m^2$/g). While both of these were lower than the surface area of a commercially activated carbon, the latter fell within the expected range of commercial products, thus suggesting an effective means of producing activated carbon while reducing sewage waste disposal costs.

**Key Words:** Activated carbon, humic acid, pyrolysis, adsorption.

## 1. INTRODUCTION

Municipal and industrial plants in Turkey, and other countries, consume large volumes of water for various purposes. The water quality that is required for a plant varies with the specific purpose, and so the quality of water that is discharged from a plant. Increasing demands on existing water supplies place pressure on wastewater facilities to adequately treat and release large amounts of water. The quality of natural waters varies with source (e.g., groundwater aquifer or surface water body), but all waters contain some minerals, trace elements and organic substances, and are treated to different levels of purity depending upon their intended use.

Humic substances are abundant organic compounds found in sediment, soil and even in rocks that are formed from the decay of organic molecules from vegetation, animals, and microbes. Not surprisingly, coal, which is formed when plant material is compressed under extreme pressure in a low-oxygen environment, can be high in humic substances. Water, flowing through coal seams, can accumulate and carry humic substances to groundwater sources and surface water bodies. The nature of these substances can vary widely, but in general they can be defined as acidic, hydrophilic and complex materials, including humic acids, fulvic acids and humins. Humic acids are common in natural waters and pose no risk to humans or animals in their unaltered states.

Humic substances can react with chlorine to produce carcinogens in drinking water. However, chlorination can cause the formation of potentially toxic and carcinogenic molecules [1]. Removing humic substances from water prior to disinfection with chlorine will prevent the formation of post-reactive molecules, such as trihalomethanes, and thus reduce the potential risk to human health.

On water treatment plants, humic substances are removed between 20 and 50% with conventional drinking water treatment processes of coagulation, settling and sand filtration [2]. Activated carbon can be used as an effective treatment method to remove humic substances from water prior to disinfection by chlorination. For removal of humic substances, the adsorption process is widely used with activated carbon and other absorbents can be chosen from different raw materials such as agricultural wastes, sewage sludge, ashes etc. Agricultural wastes and sewage sludge, for example, can be pyrolyzed under controlled conditions with/ without some chemical additives to be converted into useful adsorbent materials. This conversion would offer the combined benefits of reducing the volume of agricultural waste and sewage sludge, while producing a valuable, low-cost adsorbent [3].

Activated carbon is the most preferred adsorbent and has been used with great success. However, it is expensive and its regeneration and reuse makes it more costly. Because of these difficulties, various adsorbents and methods have been tested for humic acid removal. These include bentonite [4], ozonation and biofiltration [5], Montmorillonite [6], ultra and nanofiltration [7], coagulation and Ion exchange [8], activated sludge biomass [9], clay [10], chitosan-coated granules [11], animated polyacrylonitrile fibers [12], silica [13].

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*Address correspondence to this author at the Department of Environmental Engineering, Faculty of Engineering, Istanbul University, 34320, Istanbul, Turkey; Tel: +902124737070; Fax: +902124737180;
E-mail: guneysu@istanbul.edu.tr

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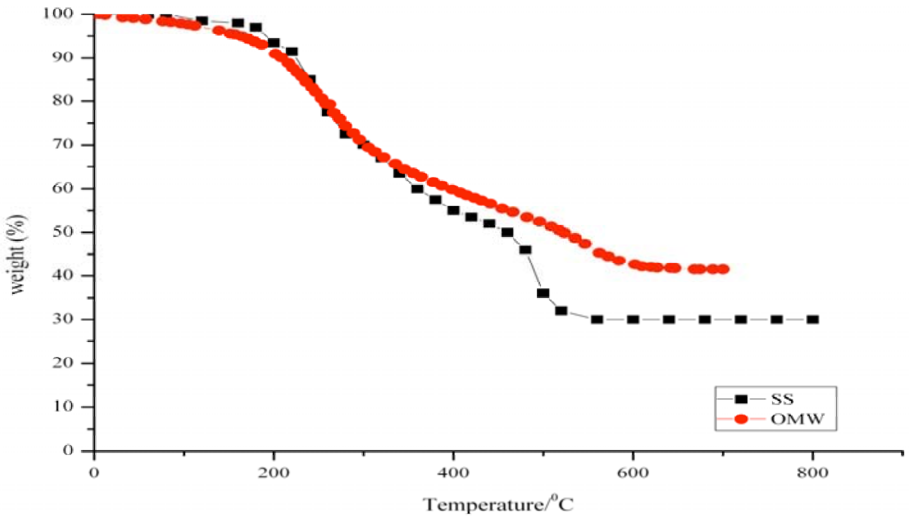

**Fig. (1).** Thermo gravimetric curves of sewage sludge (SS) and olive mill waste (OMW) samples.

**Table 1. C, H, N, Moisture and Ash Contents of the Sewage Sludge, the Olive Mill Waste Raw Material (% Oven-Dried Mass) and Powdered Activated Carbon (PAC)**

| | Carbon (%) | Hydrogen (%) | Nitrogen (%) | Ash (%) | Moisture (%) |
|---|---|---|---|---|---|
| Olive Mill Waste | 45.64 | 6.31 | 1.42 | 14 | <5 |
| Sewage Sludge | 48.8 | 6.7 | 9.5 | 9.4 | 10 |
| PAC | 87.51 | 0.35 | 0.2 | <1 | <5 |

The goal of the present study was to investigate the potential application of the adsorbents, derived from agricultural waste biomass and sewage sludge to humic substance adsorption. The effects of preparation parameters such as the concentration of the activating agent $ZnCl_2$, heating temperature and heating rate were studied in order to identify an optimum condition for adsorbent production. Surface area, physical morphology and adsorption characteristics of the adsorbent were investigated. Thermogravimetric method has been used as the main technique for studying the processes occurring in tar and char pyrolysis and activation, and to determine the activation conditions [14]. For comparison, all characterization tests were also applied to a commercial powdered activated carbon (Reidel-de Haen-Charcoal activated powdered, pure) which has a Brunauer-Emmett-Teller (BET) surface area of 1120 $m^2/g$.

## 2. MATERIALS AND METHODOLOGY

The olive mill waste used in this study was collected from the city of Balikesir in the Aegean region, and dried at 103-105 °C. Sewage sludge samples were collected from a alcohol industry waste water treatment plant and two samples were crushed and sieved to a uniform size of 0.5 to 2.0 mm before being stored until carbonization.

### 2.1. Preparation of Adsorbent

The olive mill wastes (OMW) were a mixture of pulp and olive stones. Both the olive mill wastes (OMW) and the sewage sludge (SS) samples were rich in carbon and low in ash content (Table **1**). The TG analysis of sewage sludge and olive mill wastes was given in Fig. (**1**). Both these properties make it suitable for carbonization [15].

The sewage sludge sample was directly pyrolyzed for 2 hours, at 500 °C with 2M $ZnCl_2$ solution as an activating agent addition, under a flow rate of 0,1 $m^3/h$ nitrogen [16]. The olive mill waste was pyrolyzed for 2 hours, at 700°C, with 1.0 M zinc chloride solution as an activator, under a flow rate of nitrogen [17]. The different pyrolysis temperatures were 500, 600, 700 and 800ºC, with a heating rate of 10ºC/min. The samples were characterized quickly and accurately using a porosimetry analyzer (Micrometrics FlowSorb II 2300 system).

The olive mill waste was first reacted with different volumes of a zinc chloride solution for 24 hours, then pyrolyzed and soaked for 2 h, at 700°C and analyzed. After carbonization, these pyrolyzed cokes were washed with a 3 M HCl solution to remove zinc chloride from porous structures [17]. Then they were rinsed with distilled water several times for removing HCl and dried in an oven at 103-105 °C.

Specific surface areas of the products were determined by a surface area analyzer (Micromeritics Flowsorb II-2300) on a nitrogen adsorption principle (at 77° K). The specific surface area was calculated using the BET equation.

### 2.2. Humic Acid Solution

A humic acid solution was prepared in the laboratory using the following chemicals: 0,1 g. of Humic acid (Fluka-

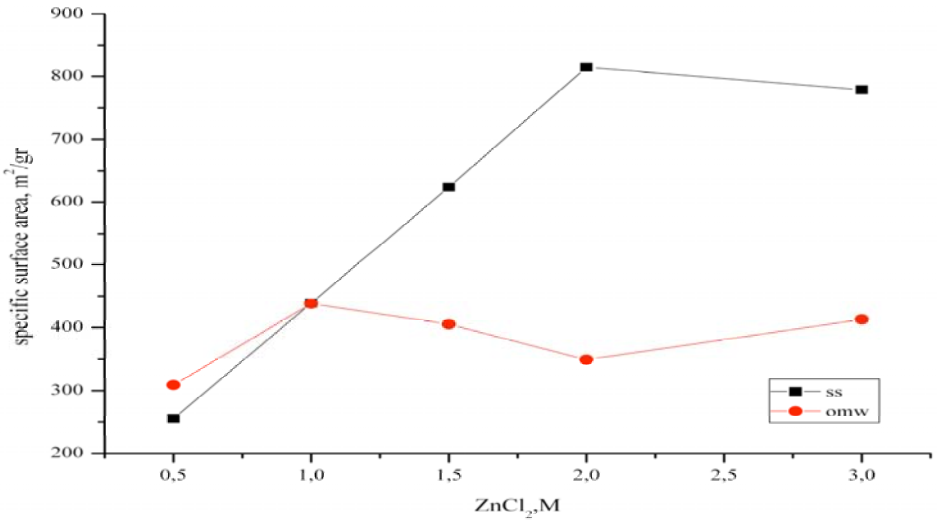

**Fig. (2).** Specific surface areas of pyrolyzed cokes; sewage sludge (SS), olive mill waste (OMW).

53680) dissolved in 0,1 N sodium hydroxide (Reidel-de Haen-06203) and completed to 1L. Different humic acid concentrations were prepared daily and kept at 25°C in a dark place.

### 2.3. Adsorption Tests

Adsorption tests were conducted at 25°C in a batch system on a shaker table. One-hundred milliliters of a humic acid solution was combined and shaken with 0.1 g of pyrolyzed coke at 160 rpm. Four different humic acid concentrations were tested: 10, 20, 30 and 40 mg/L. Spectral analysis results were obtained using a UV spectrophotometer at 242 nm; the humic acid concentrations were calculated from the calibration equation. Scanning electron microscopy (SEM) was used to observe the surface morphology of the adsorbent derived from olive wastes and sewage sludge samples. Micrographs were taken to document absorbent appearance.

Batch adsorption tests were conducted to determine the reaction rate and to gather equilibrium data. The adsorption performance of the adsorbent was verified by conducting humic acid-adsorption tests under laboratory conditions.

The adsorption data were applied to the Freundlich and Langmuir isotherms which were an empirical equation employed to describe heterogeneous systems. Freundlich isotherm was characterized by the heterogeneity factor 1/n.

$$\log x/m = \log k_f + 1/n \log C_e \qquad (1)$$

Where x is the amount of the adsorbed solute (mg), m is the mass of the adsorbent (g), $C_e$ is the equilibrium concentration (mg/L), 1/n is the slope, showing the variation of the adsorption with concentration, and $k_f$ is intercept, showing the adsorption capacity of the adsorbent.

Also, Langmuir isotherm is represented by the following equation;

$$C_e/q_e = 1/(Q_0.K_L) + (1/Q_0).C_e \qquad (2)$$

Where $q_e$ and $C_e$; are defined, as the amount of humic acid adsorbed and equilibrium of liquid-phase concentration, respectively.

## 3. RESULTS

### 3.1. Production of Activated Carbons

For the two wastes; olive mill waste samples and the sewage sludge samples, it was found that pyrolysis temperature was important in absorbent development (Fig. **2**). Low heating temperature produced adsorbents with poorly-developed porosity. Elevating the heating temperature increased the product-specific surface area, and the data also indicate that temperatures above 700 °C can lead to a small decrease in porosity. This showed that there is no the relationship between the heating rate and the absorbent surface area.

Specific absorbent surface area from the olive mill waste product increased with increasing $ZnCl_2$ concentrations (Fig. **2**). The highest surface area of the olive mill waste products (437.92 $m^2/g$) resulted from the addition of 1.0 M $ZnCl_2$. The BET surface area of the activated carbon derived from sewage sludge was approximately 814.48 $m^2/g$. and the BET surface area of the commercial product was 1150 $m^2/g$.

The SEM micrographs of the olive-waste samples at 1000x magnification were illustrated in Fig. (**3**). Pores of different sizes and shapes have been observed. On the walls of the large pores, some smaller pores were also presented. The large and small pores connect and intersect, forming an advanced pore structure system with substantial surface area (Fig. **3D**).

### 3.2. Aqueous Adsorption Tests

Fig. (**4**) represents the percentage adsorption of humic acid solutions by three types of powdered activated carbons evaluated in this study.

Fig. (**5**) describes the Langmuir adsorption model, but the adsorption studied in this paper couldn’t be applied to the Langmuir model. Linear plots of log (x/m) versus log $C_e$ showed that the adsorption follows the Freundlich isotherm

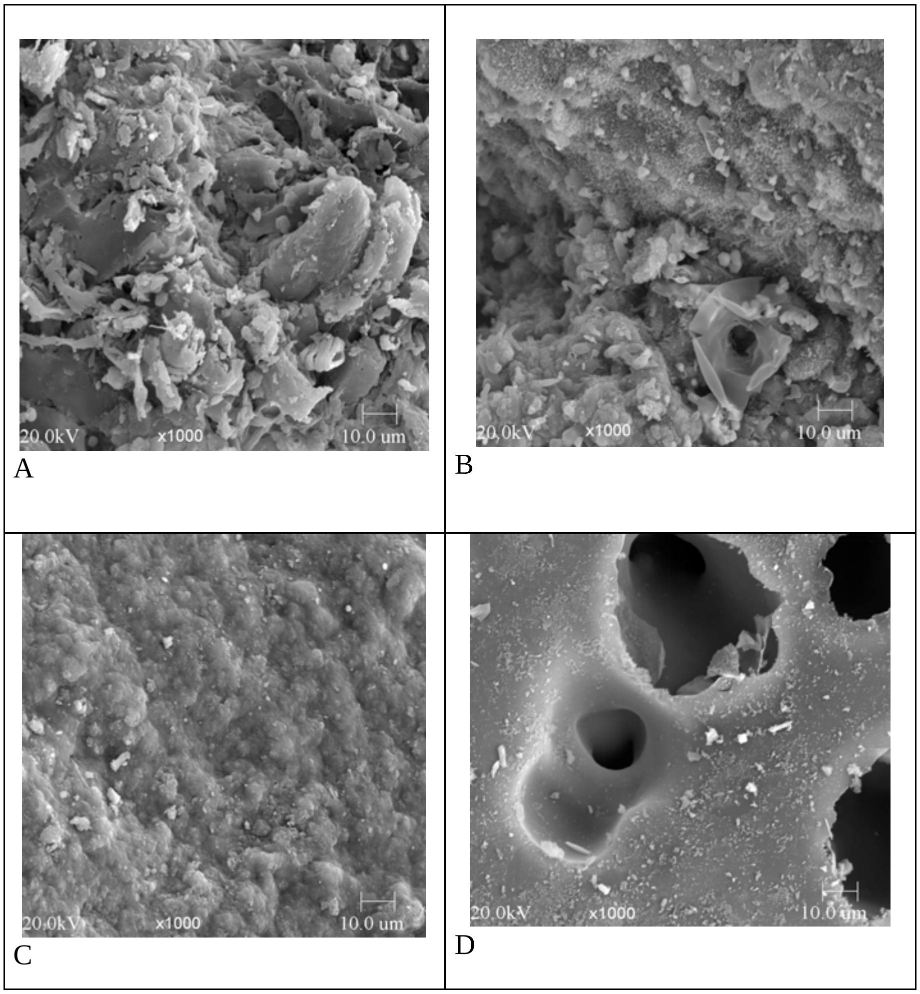

**Fig. (3).** Scanning electron microscopy (SEM) micrographs for (**A**) olive mill waste, (**B**) olive mill waste pyrolyzed (x1000), (**C**) sewage sludge and (**D**) sewage sludge pyrolyzed (x1000).

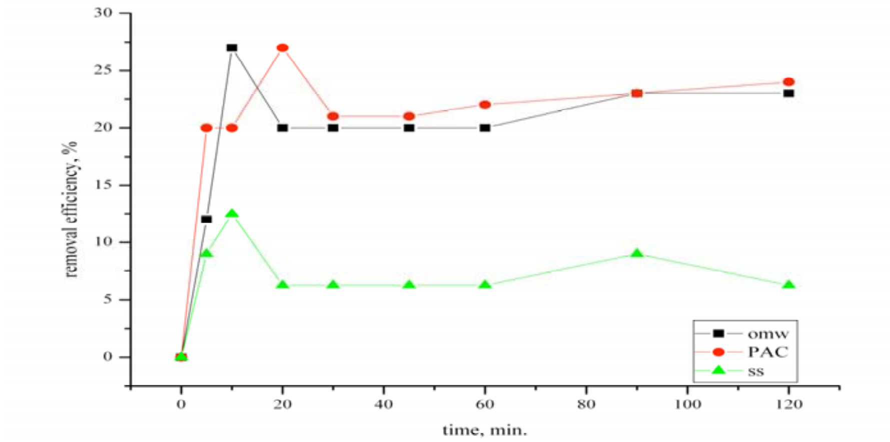

**Fig. (4).** Adsorption of humic acid by olive mill wastes (OMW), sewage sludge (SS) and powdered activated carbon (PAC).

model (Fig. **6**). $K_f$ and n values derived from the Freundlich plots (Fig. **6**) were presented in Table **2**. These data showed that, in all sorption systems, the value of n is defined as $1 < n < 10$, and beneficial adsorption was indicated for all adsorption tests.

## 4. DISCUSSION AND CONCLUSION

In summary, we can conclude that the composition of thermal structure began at nearly 200°C, and ended at 500°C and 700°C for sewage sludge and olive mill waste, respectively. The nitrogen atmosphere pyrolysis conditions

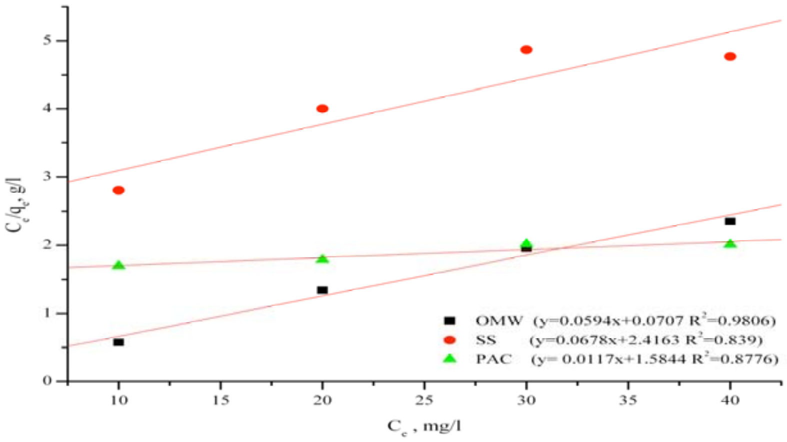

**Fig. (5).** Langmuir isotherm of humic acid adsorption by pyrolyzed coke; olive mill waste (OMW), sewage sludge (SS), powdered activated carbon (PAC).

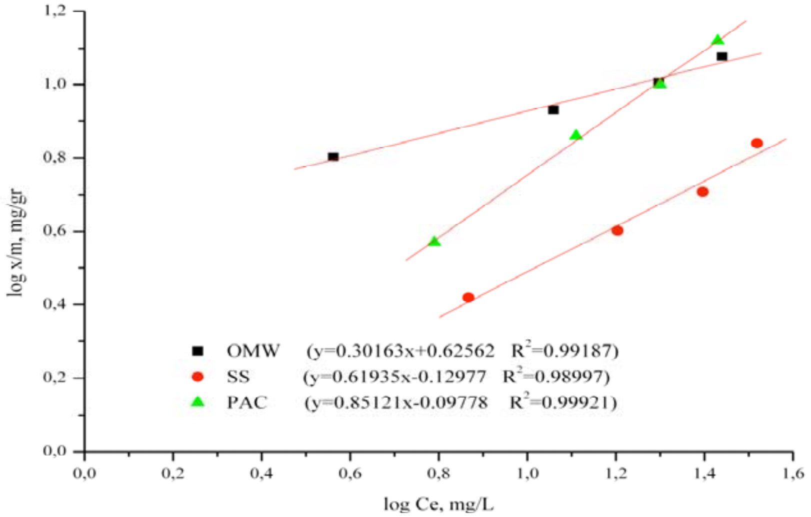

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**Fig. (6).** Freundlich isotherm of humic acid adsorption by pyrolyzed coke; olive mill waste (OMW), sewage sludge (SS), powdered activated carbon (PAC).

**Table 2. $K_f$ and n Freundlich Values of Adsorbents**

| Adsorbent | Freundlich Isotherm | | | Langmuir Isotherm | | |
|---|---|---|---|---|---|---|
| | $K_f$ | n | $R^2$ | $Q_0$ (mg $g^{-1}$) | $K_L$ (l $mg^{-1}$) | $R^2$ |
| OMW | 4.22 | 3.31 | 0.99 | 16.84 | 0.84 | 0.98 |
| SS | 0.74 | 1.61 | 0.98 | 14.75 | 0.028 | 0.83 |
| PAC | 0.80 | 1.17 | 0.99 | 85.47 | $7.4.10^{-3}$ | 0.87 |

materialized the cokes into fine commercial ones. The surface areas of three types of activated carbons (ACs) derived from olive mill wastes, sewage sludge and a commercial product, were evaluated. All three ACs possessed substantial surface area and pore volumes. Of particular note, was the AC derived from sewage sludge, activated by 2M $ZnCl_2$ and pyrolyzed at 500°C for 2 h. The specific surface area of this AC was 814.48 $m^2$/g and was comparable to commercially-available ACs with surface areas of 600 to 1100 $m^2$/g [16]. Despite the lower surface area of the AC produced from olive mill wastes, it nevertheless has a substantial removal capacity [17]. However, production of AC from sludge has two distinct advantages in that it reduces or eliminates disposal issues and, as a result, ameliorates the problem of increasing disposal costs.

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