Development of biochar sorbents from food-industry by-products for the removal of phenanthrene and mercury from aqueous solutions

S. Valili[1], A. Maneta[1], I.D. Manariotis[2*], and H.K. Karapanagioti[1]

[1]Department of Chemistry, University of Patras, Patras 26504, Greece
[2]Environmental Engineering Laboratory, Department of Civil Engineering, University of Patras, Patras 265 04, Greece
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*Presenting author e-mail: idman@upatras.gr

Abstract

The production of added value products such as biochars from food-industry by-products is a sustainable idea. These raw materials not only are free of charge but their pyrolysis will help solve management problems. The objectives of the present study are (a) to characterize the developed materials for their properties that affect sorption such as surface area, grain size, total organic carbon, etc., and (b) to evaluate the ability of these biochars to remove pollutants, and more specifically, phenanthrene and mercury, from aqueous solutions. All biochars presented better sorption capacity than the raw biomass (e.g. malt spent rootlets). The values of maximum sorption capacities (q_{max}) are rather satisfactory Based on the results, biochar is suggested as an effective solution for the decontamination of water from phenanthrene and mercury.

Keywords: Biochars; biomass; valorization; sorbents; water and wastewater treatment.

1. Introduction

Biomass management is associated with several problems since its disposal on soil results into the leaching of organic matter and the increase of organic loading in groundwater. So far, the main venue for biomass produced by food industries as a byproduct is the use as feedstock or in composting. Recently, there is increasing interest in the utilization of biomass by-products of food industry and biomass [1-4]. The use of these by-products for the production of biochar is considered a mitigation measure for global warming once it is used as a soil amendment. In addition the use of biochar as an added value product, such as sorbent or catalyst, is desirable and could be more profitable and thus, more sustainable than its simple addition to soils [5]. Producing added value products such as biochars from food-industry by-products is a sustainable idea. These raw materials not only are free of charge but their thermal treatment will help solve management problems.

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants due to their mutagenic and carcinogenic properties even at low concentrations [6-7]. Phenanthrene, a three-ring polycyclic aromatic compound is used as a model nonpolar organic pollutant. Mercury, on the other hand, is one of the heavy metals of particular concern due to its toxicity even at relatively low concentrations. Mercury and its compounds are classified among priority hazardous compounds according to the European Union (EU) legislation [8].

The most common physicochemical processes to remove mercury from water are coagulation, chemical precipitation, reverse osmosis, adsorption, ion exchange, and solvent extraction [5]. In our previous work raw malt spent rootlets, chemically modified and pyrolyzed were successfully used for the removal of mercury [5] and phenanthrene [9] from aqueous solutions.

The objective of the present study was to evaluate the potential use of various food industries (brewering, coffee, wine, and olive oil) by-products and their biochars for the removal of organics and metals from aqueous solutions. The specific objectives were (a) to characterize the developed materials for their properties that affect sorption such as surface area, grain size, total organic carbon, etc., and (b) to evaluate the ability of these biochars to remove pollutants, and more specifically, phenanthrene and mercury, from aqueous solutions. The significance of sorbents properties that affect sorption such as surface area, grain size were also evaluated.

2. Materials and Methods

Raw materials for biochar production used in this study included by-products from brewering, coffee, wine, and olive oil industries. Biochars were prepared in specialized containers using oxygen-limited pyrolysis at 850^{o}C. Total organic carbon (TOC) content was measured using an Elemental Analyzer. Surface area and porosity were measured using nitrogen adsorption combined with the BET equation.

Batch sorption experiments were performed at room temperature with nine different biochar samples and various phenanthrene or mercury ($HgCl_2$) aqueous concentrations ranging from 5 to 280 mg/L, respectively. The sorption isotherms were determined after contact time of 24 hrs and/or 7 days for phenanthrene and after 24 hrs for mercury. The amount of biomass (m=0.003±0.0003 g) was stable for all the experiments. Phenanthrene was analyzed with a fluorescence detector [9] whereas mercury was measured following a colorimetric determination with Michler's thioketone method and a spectrophotometer [4-5]. Calibrations were performed each day prior to sample measurements. For phenanthrene experiments the pH was around 7 whereas for $HgCl_2$ solution was 5 ± 0.5 as it is considered to be the optimum pH for the removal of mercury according to past surveys [4-5].

In this study, both linear and non-linear isotherms have been observed. For linear isotherms the sorption distribution coefficient (K_d) is equal to:

$$K_d = \frac{Q_e}{C_e} \tag{1}$$

where, Q_e is the quantity of phenanthrene (μg/kg) or mercury (mg/g) sorbed per mass unit of biochar, and C_e is the phenanthrene (μg/L) or mercury (mg/L) concentration in water after 7 days. Q_e is calculated as follows:

$$Q_e = \frac{(C_o - C_e)V_l}{m_s} \tag{2}$$

where, C_o is the initial phenanthrene concentration (measured through blank samples), V_l is the volume of the solution, and m_s is biochar mass in each vial.

3. Results

3.1 Materials Characterization

Table 1 presents the characteristics of the various biochars produced from different materials. TOC content in biochars ranged from 50 to 84%. Surface area measurements resulted in values ranging between 230 and 660 m^2/g. The pore volume ranged from 0.01 to 0.18 cm^3/g.

Table 1. Characteristics of biochars produced from different raw materials.

Sorbent	TOC (%)	S.A. (m^2/g)	P.V. (cm^3/g)
1.18 mm < MSR < 2.36 m	52	570	0.11
1.18 mm < MSR < 2.36 m	50	400	0.18
MSR powder	52	410	0.10
Espresso coffee	71	490	0.04
Espresso coffee	64	660	0.07
Grape seeds	71	340	0.05
Olive core	84	410	0.01
Grape stalks	61	280	0.07
Grape husks-seeds	51	230	0.03

Note: MSR: malt spent rootlets; S.A.: surface area; P.V.: pore volume.

3.2 Phenanthrene Removal

For phenanthrene, biochars presented both linear and nonlinear isotherms (Freundlich exponent, N=0.25 to 0.98). In all cases, the concentration of phenanthrene on the solid (Q_e) was at least 5 orders of magnitude higher than the aqueous phenanthrene concentration (Figure 1). Also, as can be seen in Figure 1, the concentration of phenanthrene on the solid was 1 to 2 orders of magnitude higher than that of biosorbents (e.g. malt spent rootlets, MSR). Since raw MSR demonstrates a TOC of 40% and a surface area equal to 0.18 m^2/g [9], the increased phenanthrene sorption by biochars compared to MSR can be attributed to increased TOC and surface area for the biochars.

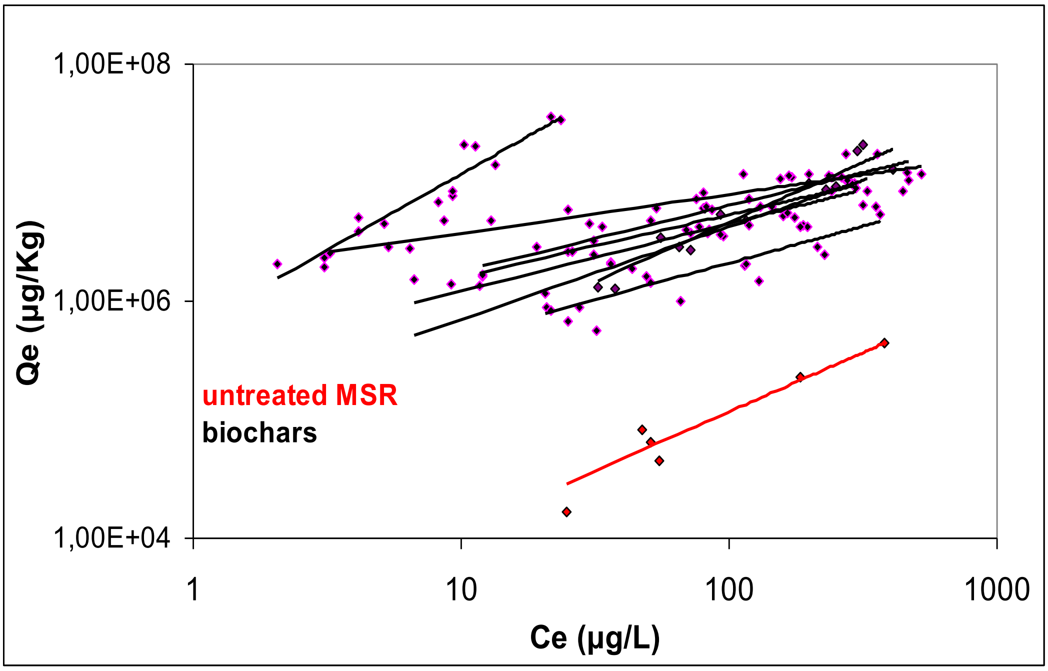

Figure 1 Phenanthrene sorption isotherms for untreated malt spent rootlets (MSR) and biochars.

Phenanthrene sorption capacity increased by at least a factor of 2 between 1 and 7 days. For example in Figure 2, the Q_e of the biochar made from grape seeds increased by a factor of 43 between the 1st and the 7th day of contact.

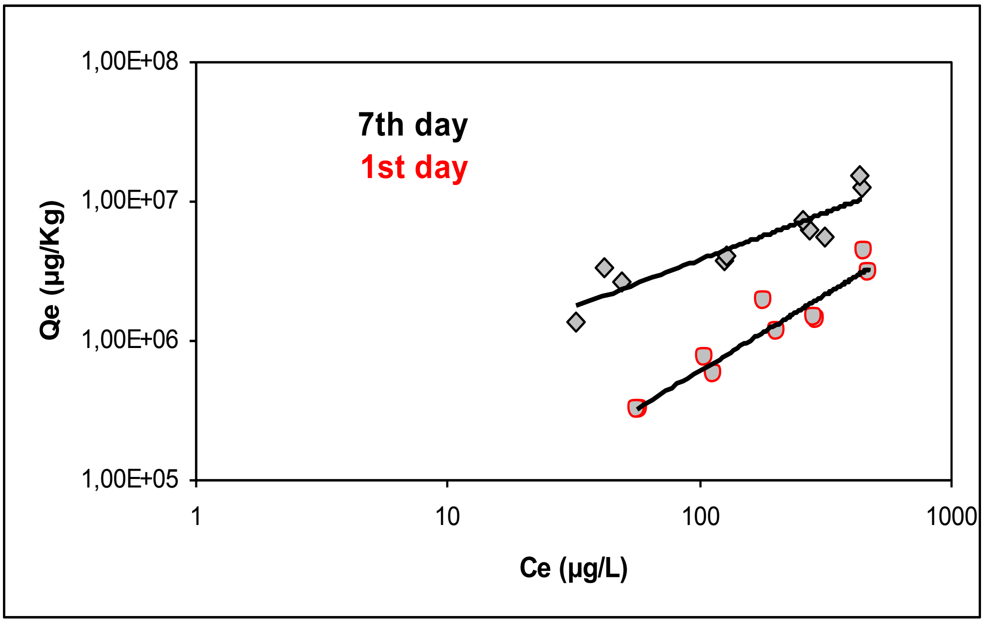

Figure 2 Phenanthrene sorption isotherms for biochar made from grape seeds, after 1 and 7 days of contact.

3.3 Mercury Removal

For mercury, the maximum biochar sorption capacity (q_{max}) is between 70 to 205 mg Hg (II)/g biochar. The biochars derived from malt spent rootlets and coffee residues present higher values of

q_{max} (represented by the lines with the lower slopes in Figure 3) while those derived from wine factory by-products present lower values (lines with high slopes in Figure 3). Also, the pH of the samples increased up to two units after 24 hours. Parameters such as specific surface, the raw material, micropores, and the carbon content affect the ability of biochars to remove mercury. The percentage of mercury removal for concentrations C=50 mg/L is 52%. In conclusion, the values of q_{max} are rather satisfactory.

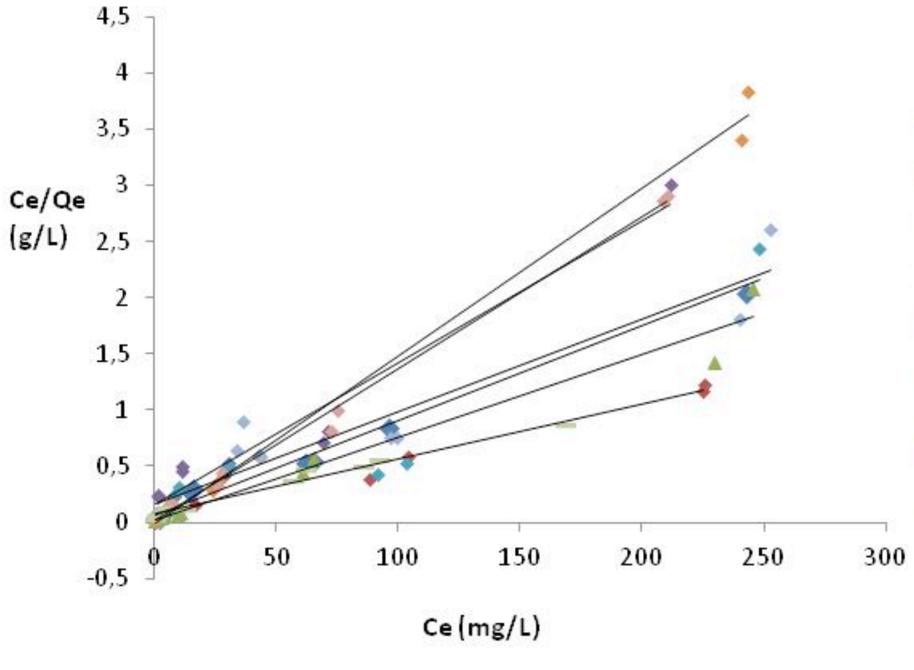

Figure 3 Mercury sorption isotherms for biochars

4. Conclusions

The use of biochars produced from food-industry by-products to remove pollutants from water is a cost-effective method. The biochars are low-cost materials and have low environmental impact. Moreover, pyrolysis method is simple and environmental-friendly, without using chemical treatment. In most cases for phenanthrene, biochar sorption is 1-2 orders of magnitude higher than that of biosorbents (e.g. malt spent rootlets), respectively. For mercury, biochar sorption is double that of the biosorbents. Based on the results, biochar is suggested as an effective solution for the decontamination of water from phenanthrene and mercury.

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