Assessment of pistachio shell biochar quality and its potential for adsorption of heavy metals

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2nd INTERNATIONAL CONFERENCE on Sustainable Solid Waste Management

12–14 June 2014

Outline

In the present study pistachio shells obtained from Aegina island, Greece, were subjected to pyrolysis for the production of biochar

- Biochar from pistachio shells
- Methodology
- Characterization of biochar
- Use of analytical techniques, namely TG, XRD, FTIR and SEM
- Adsorption potential of biochar
- Conclusions

Biochar

- Biochar is a carbon rich, fine-grained and porous material which is produced by heating organic matter at temperatures not exceeding 700 ^{o}C
- Several thermochemical processes, such as slow or fast pyrolysis can be used for the production of biochar from agricultural wastes
- Pyrolysis involves thermal treatment of biomass at temperatures >400 ^{o}C in a low oxygen atmosphere
- Due to its chemical and biological stability, when biochar is applied to agricultural land may improve soil fertility, maintain sustainable production and reduce contamination of streams and groundwater

Biochar from pistachio shells

- Biochar can be produced in every country using biomass from biowaste (which includes biodegradable municipal and agricultural waste)
- In the Mediterranean region the life cycle of pistachio, which is produced in orchards of *Pistacia vera L.*, results in the production of considerable amounts of by-products
- Only in Greece, the primary processing of these nuts results in over 7000 tons of by-product streams (hulls and shells) which are more than 75% of the harvested crop
- Traditionally, these by-products are used either as animal feed, fuel for energy generation (mainly in the US), soil amendment or are discarded as waste

Methodology$_1$

- Roasted and light salted pistachio shells (PI) were obtained from Aegina island, Greece
- PI was soaked for 6 hours in warm water (60 ^{o}C) to remove most salt and then dried for 24 hours
- Pyrolysis of small quantities, e.g 50 g, of PI was carried out in a modified laboratory furnace at 250-650 ^{o}C (heating rate 10 $^{o}C \cdot min^{-1}$, retention time 60 min)

Methodology$_2$

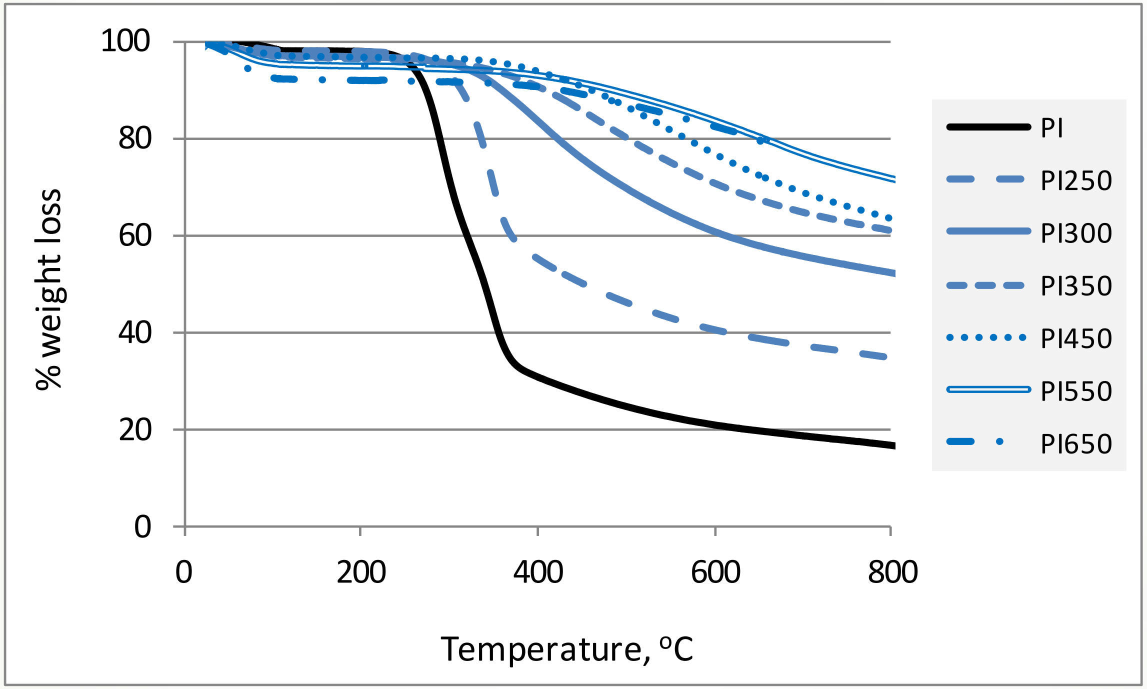
- Various parameters have been determined in biochars including pyrolysis yield, pH, EC, C-H-N-S, porosity, volatile matter, char, fixed carbon and ash content
- TG/DTG, XRD, FTIR and SEM analyses have been used
- Adsorption experiments were carried out; four solutions with various concentrations, namely 15, 45, 70 and 150 $mg \cdot L^{-1}$ Pb and Cu and four concentrations of the adsorbents (**PI, PI300, PI550**), namely 1, 2, 5 and 10 $g \cdot L^{-1}$, were used

Characterization

Table 1. Characterization of pistachio shell (PI) and biochars PI250, PI300, PI350, PI450, PI550 and PI650

	PI	*PI250*	*PI300*	*PI350*	*PI450*	*PI550*	*PI650*
y_P %	-	72.9	49.9	31.6	31.4	28.4	26.0
pH	4.25	4.68	4.96	5.11	6.71	7.15	8.81
EC, mS/cm	7.7	13.1	13.7	21.5	25.9	29.7	33.9
VM, %	86	70.9	49.2	48.1	44.1	28.3	13.9
Char, %	14	29.1	50.8	51.9	55.9	71.7	86.1
FC, %	12.4	27.1	49.0	50.2	54.2	69.9	84.4
Ash, %	1.6	2	1.8	1.7	1.7	1.8	1.7
Porosity, %	15.2	22.3	26.0	27.9	29.6	32.5	34.1
% C	45.93	54.20	66.67	69.98	75	77.25	79.34
% H	6.04	5.34	4.16	3.31	2.84	2.14	1.32
% N	0.42	0.37	0.34	0.23	0.21	0.18	0.05
% O	48	40	29	26	22	20	19

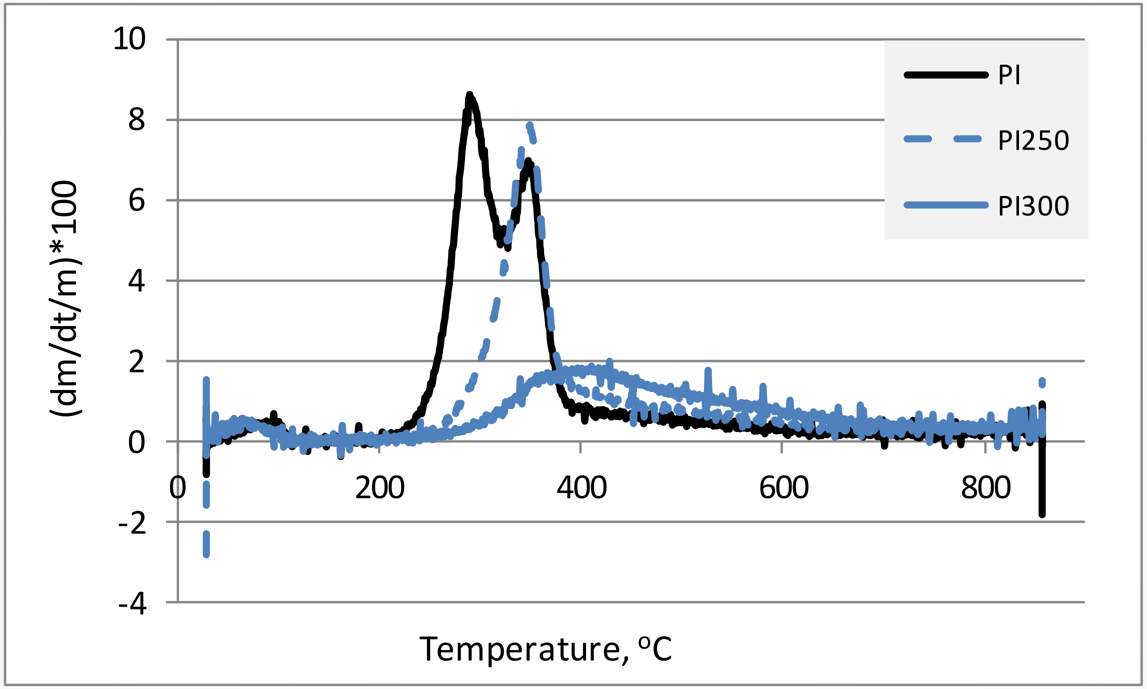
TG analysis



TG curves of weight loss versus temperature

- For all samples, the weight loss during heating up to 250 °C does not exceed 8%. A sharp weight loss is shown for PI and biochar **PI250** between 300 and 400 °C, while for biochars **PI300-PI650** the weight loss is linear and smooth at temperatures higher than 300 °C.

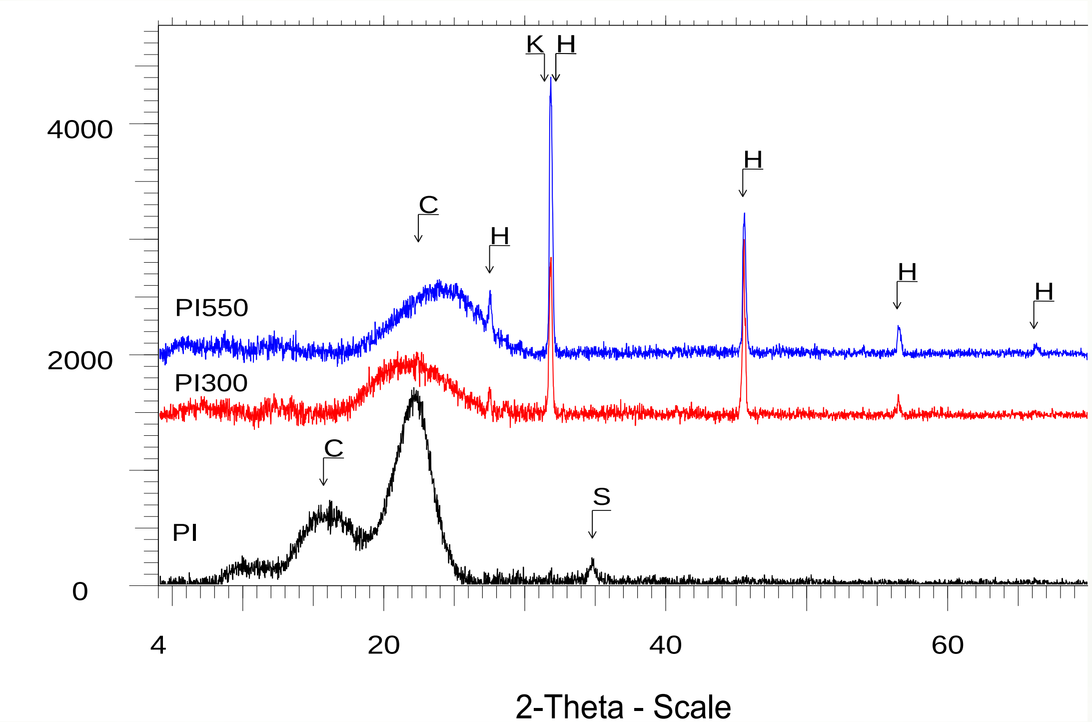
DTG analysis



DTG curves of weight loss rate versus temperature

- Two distinct peaks are clearly shown in the DTG curve of PI, which are typical for pyrolysis of lignocellulose materials (decomposition of hemicellulose and cellulose). The gradual decomposition of lignin over a wider temperature range (275-500 °C) is represented by the flat section.

XRD analysis

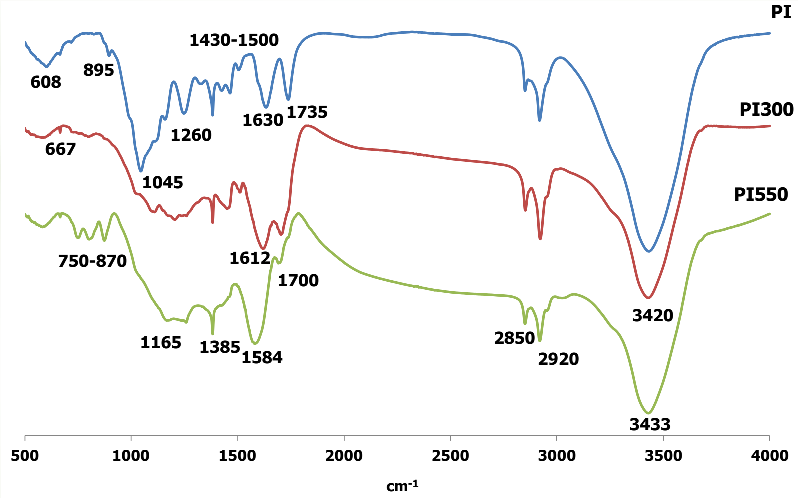


XRD patterns of pistachio shells PI and biochars PI300, PI550 (C: cellulose $(C_6H_{10}O_5)_n$, H: halite (NaCl), K: kalicinite ($KHCO_3$), S: thermonatrite ($Na_2CO_3H_2O$))

- Cellulose, which is one of the important structural components of the primary cell wall of green plants, is detected in **PI, PI300** and **PI550.** Elevated background between 16 to 26^o 2-theta, is due to the presence of organic matter. Halite is present in biochars **PI300** and **PI550**, as a residual phase.

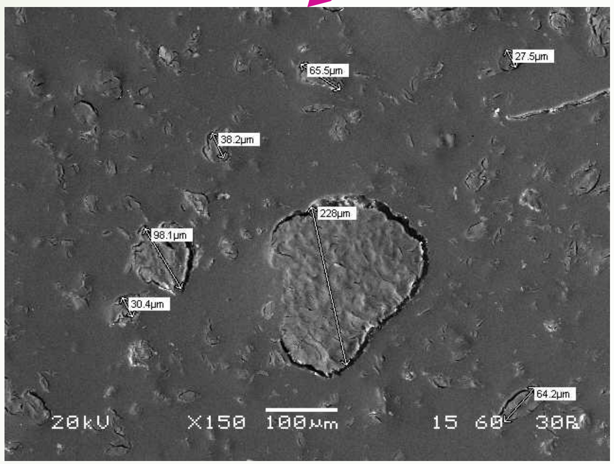
FTIR analysis

Band number, cm^{-1}	Assignment
3433, 3420	Hydroxyl group (−OH) stretching
2850, 2920	Aliphatic C−H deforming vibration
1735, 1700	ν(C=O) vibration in carbonyl group or presence of carboxylic bonds
1630, 1612, 1584	Aromatic C=O ring stretching (likely –COOH) or C=C stretching of aromatic groups in lignin
1500-1430	Aromatic C=O ring stretching
1385	δ(C=H) vibration in alkanes and alkyl groups
1260	C=C stretching
1045, 1165	Aliphatic ether, alcohol C−O or aromatic stretching peak, O−H deformation vibrations, b-glycosidic bond in cellulose and hemicellulose
800-600	C–H wagging vibrations

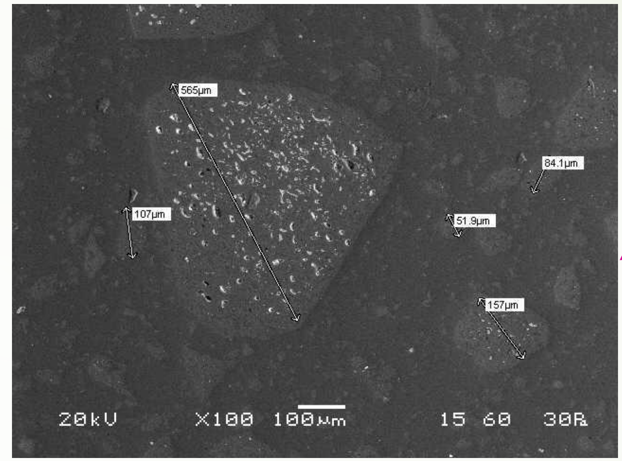


SEM analysis

the matrix of pistachio shell PI is heterogeneous containing particles with varying size

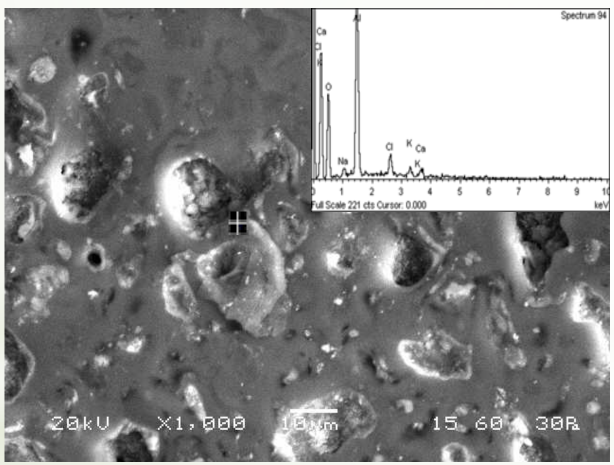


a)

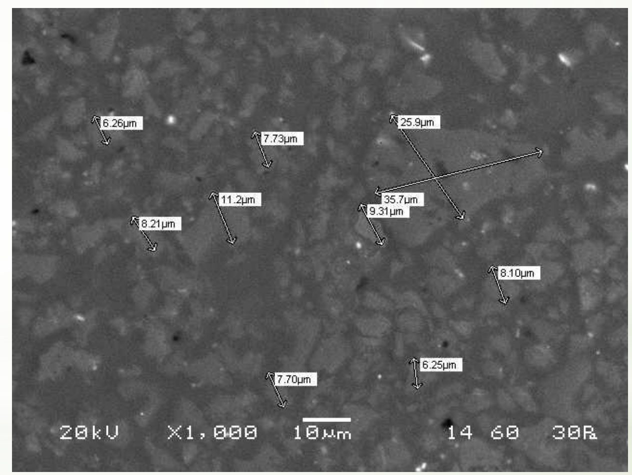


b)

some agglomeration takes place



c)



d)

a more homogenous matrix is obtained

SEM-BSI images of a) **PI (x150),** b) **PI300 (x100**), c) representative EDS analysis of the **PI300** pore structure and d) **PI550 (x1000)**

Adsorption potential of biochar[1]

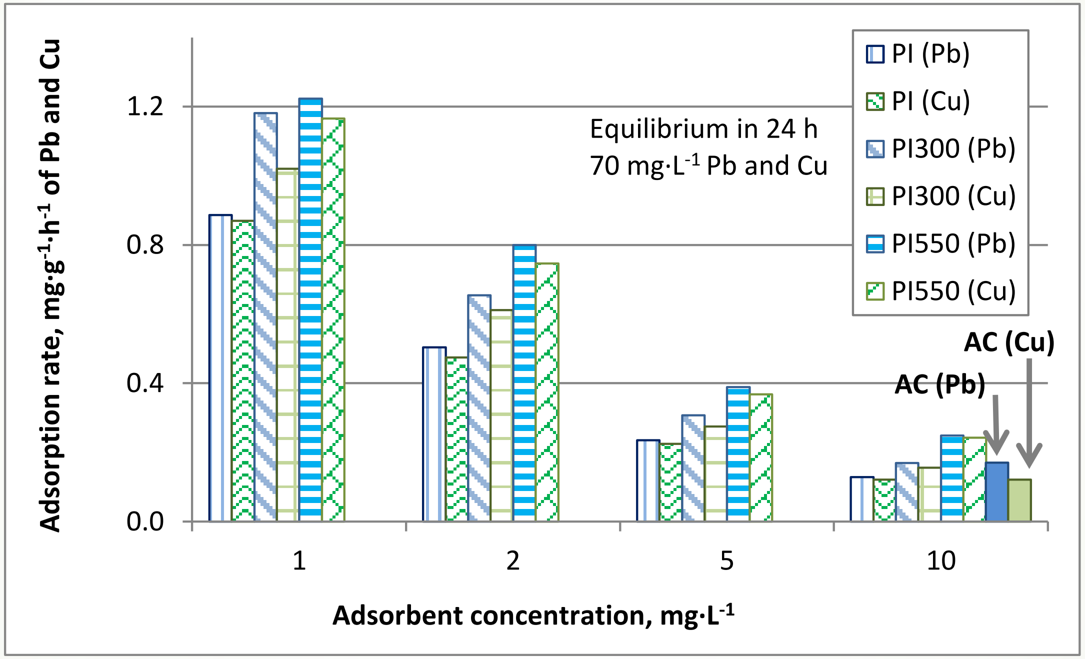
% Pb and Cu adsorption for pistachio shell PI and biochars **PI300** and **PI550** for various Pb and Cu (15, 45, 70 and 150 mg·L^{-1}) or adsorbent (1, 2, 5 and 10 g·L^{-1}) concentrations (AC: activated carbon)

Adsorbent[1]	Pb and Cu concentration (mg·L^{-1})	% Pb adsorption	% Cu adsorption	*Adsorbent*	Adsorbent concentration (g·L^{-1})	% Pb adsorption[2]	% Cu adsorption[2]
PI	15	86.2	62.4	*PI*	1	31.4	30.9
	45	75.7	42.9		2	34.7	32.7
	70	44.3	41.8		5	40.0	38.2
	150	38.3	36.7		10	44.3	41.8
PI300	15	96.9	71.2	*PI300*	1	40.0	34.5
	45	73.9	57.1		2	45.7	42.7
	70	57.1	52.7		5	52.9	47.3
	150	49.7	37.8		10	57.1	52.7
PI550	15	99.7	99.6	*PI550*	1	42.9	40.9
	45	99.1	97.6		2	53.6	50.0
	70	85.7	83.6		5	67.1	63.6
	150	77.2	62.8		10	85.7	83.6
				AC	10	57.1	41.6

Adsorption potential of biochar$_2$

- Pb is adsorbed more efficiently compared to Cu on PI and both biochars **PI550** and **PI300**, due to its larger ionic radius than Cu
- The adsorption capacity of pistachio biochars increases with increasing pyrolysis temperature
- The highest % adsorption of Cu and Pb, almost 100% for both ions, is shown for 10 $g \cdot L^{-1}$ biochar **PI550**, when the initial Pb and Cu concentration in solution was 15 $mg \cdot L^{-1}$
- Experimental data fit very well the Freundlich model

Adsorption potential of biochar[3]



Adsorption rates, $mg \cdot g^{-1} \cdot h^{-1}$, of Pb and Cu using various solution and adsorbent concentrations

- Activated carbon shows almost identical with biochar PI300 adsorption rates, 0.17 and 0.13 mg·g-1·h-1, for Pb and Cu respectively, when the initial heavy metal concentration is 70 mg·L-1

Conclusions

- The present study shows that pistachio shells can be pyrolysed for the production of biochar, that can be used both as soil amendment and adsorbent for the clean-up of solutions containing heavy metals such as Pb and Cu
- The use of analytical techniques, namely TG, XRD, FTIR and SEM, offers significant insights regarding the composition and the morphology of the produced biochars
- Pyrolysis temperature affects positively the biochar capacity in terms of Pb and Cu adsorption and subsequent removal from solutions. Biochars produced at 550 ^{o}C show high Pb and Cu adsorption capacity, which is much better than that of commercial activated carbon.

Thank you …

Acknowledgement

This research has been co-funded by the European Union (European Social Fund) and Greek National Resources through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) – Research Funding Program: THALES, Sub-project "Development of an integrated methodology for the management, treatment and valorisation of hazardous waste (WasteVal)" (code MIS 380038). Investing in knowledge society through the European Social Fund.

Project website: http://wasteval.labmet.ntua.gr/#&home

European Union European Social Fund
OPERATIONAL PROGRAMME EDUCATION AND LIFELONG LEARNING investing in knowledge society
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