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Efficient Activation and Modification of Biochar for Sustainable Water / Energy / Food Nexus

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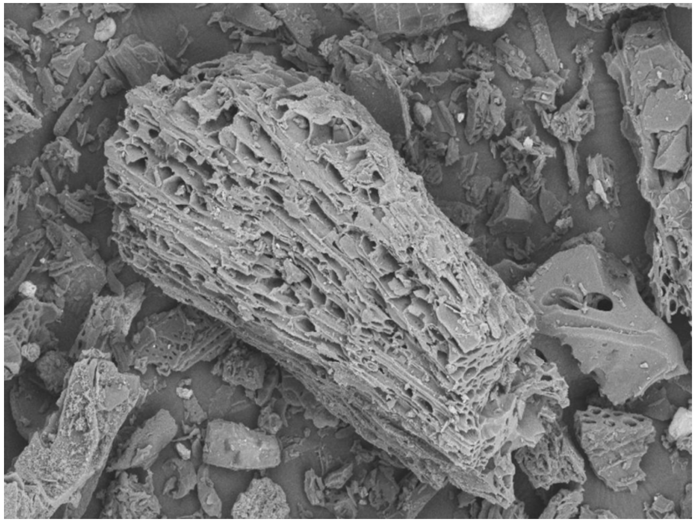
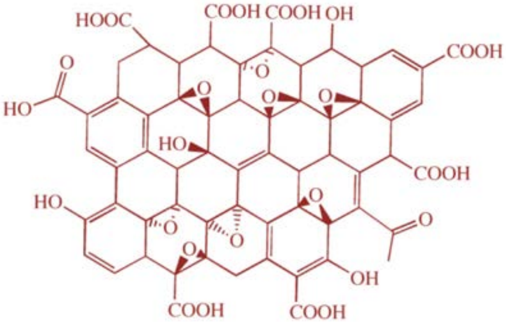




August, 2018

Outline

1. Objective

- To explore transformative routes of CO_2 fixations on different carbonaceous structure
- To develop advanced carbon modification technologies

2. Synthesis of concepts, hypotheses and demonstrations

- What is biochar?
- The effect of photo-Irradiation on biochar
- The effect of ultrasound irradiation on biochar

3. The three technological concepts derived from these demonstrations

- Efficient gasification technology
- CO_2 capture by biochar activated by low frequency ultrasound waves and functionalized with Amine
- Adsorption of Water Pollutants by Biochar Activated by Ultrasonic Treatments

Objective in Broad Sense

- To explore transformative routes of CO_2 fixations on different types of carbons as many
  - **CO_2 capture** processes, and
  - **CO_2 utilization** processes, including new **cradle-to-cradle** routes for CO_2 reuse,

involve CO_2 fixations on carbon as the first step in the process.

- Particular interests have been placed on the synergisms of **photo-** and **ultrasonic-energy** in the carbonaceous materials/H_2O/CO_2 systems.

- To develop advanced and economically feasible carbon modification technologies for sustainability in food/energy/water.

Two Routes of Special Interests

- **Photochemical route**
  - Demonstrated photochemical CO_2 fixation on carbon
  - Need to bring CO_2 to high energy levels; i.e., to create a cradle-to-cradle carbon cycle
  - Solar energy is renewable

- **Ultrasonic route**
  - Demonstrated leaching of minerals by water
  - Demonstrated water splitting to form reactive H and OH radicals
  - Demonstrated graphite oxide exfoliation

Concept 1: Reactivity of Aromatic Carbons – Reductive Photocarboxylation

Chateauneuf et al. (2002) used supercritical CO_2 in their ***reductive photo-carboxylation*** experiments, and discovered the near complete conversion and the following mechanism:

$$PAH \xrightarrow{h\nu} PAH^* + DMA \rightarrow PAH^{\bullet -} + CO_2$$

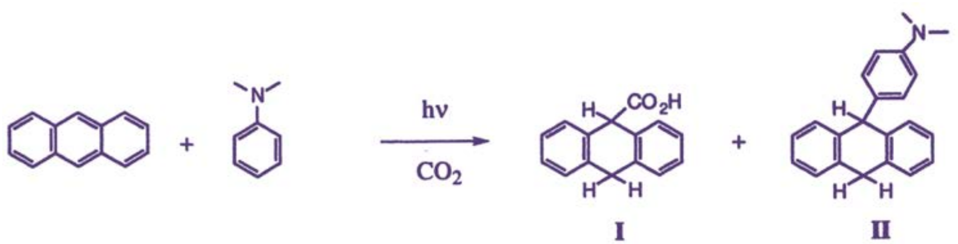
$$\rightarrow PAH^{\bullet} - CO_2^- + i\,\mathrm{Pr}OH \rightarrow H - PAH - CO_2^-$$

where *DMA* denotes N,N-dimethylaniline (an electron donor) and *i*Pr*OH* 2-propanol (a hydrogen donor), respectively.

Our Postulations:

Reductive photo-carboxylation of edge carbons of PAHs be considered as a mean to

- enhance the hydrogen content, thus the **energy content**, of the reactant,
- **capture CO_2**.



Dihydrocarboxylic acid, **I**, is the major product only when a hydrogen donor such as 2-propanol is present (Chateaunef et al., 2002).

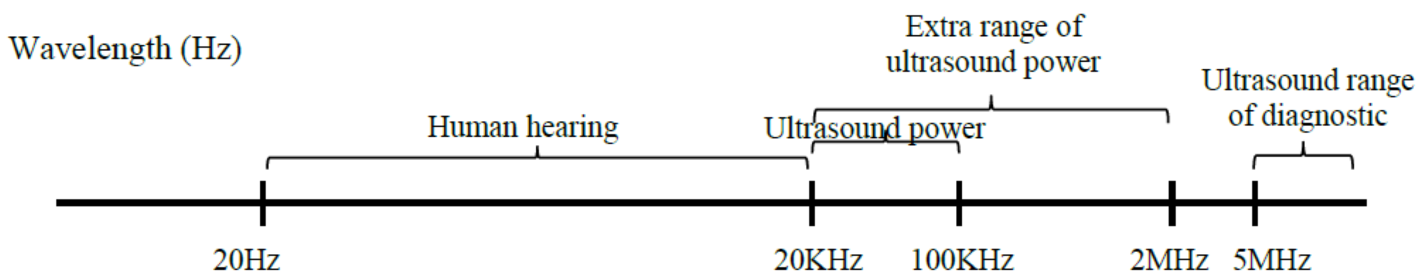
Concept 2: Ultrasound Waves

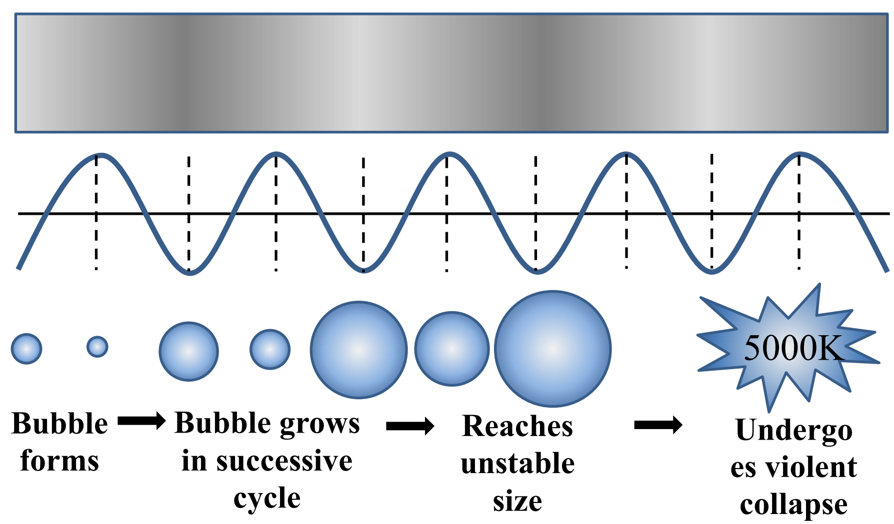
- **Ultrasound Effects**
- **Ultrasound Energy**

> Ultrasound waves are a category of acoustic waves in the form of sinusoidal pressure waves with a frequency higher than human hearing range (>20 kHz).
> Ultrasound waves have a short wavelength and high energy transmittance ability.

Cavitation Bubbles: Expansion and compression of liquid during propagation of pressure waves resulting in generation and subsequently compression of micro bubbles.

Hot Spots: A large number of localized over-heated regions named as hotspots are produced by vigorous collapses of these bubbles.

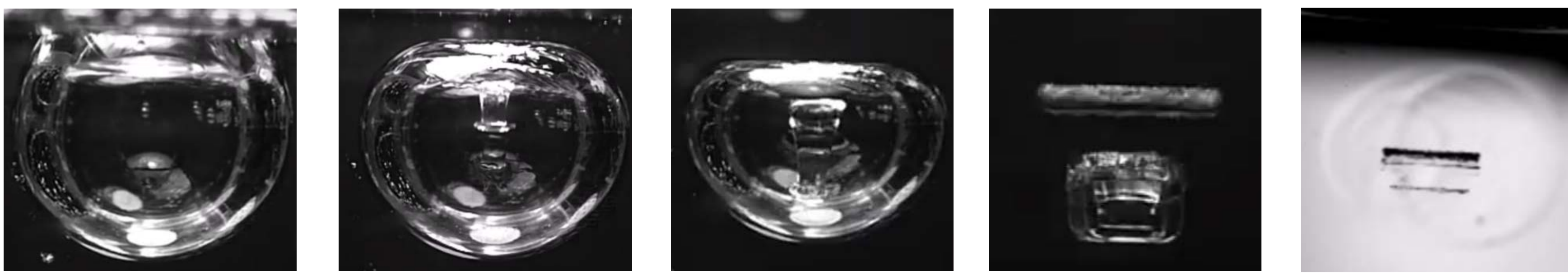


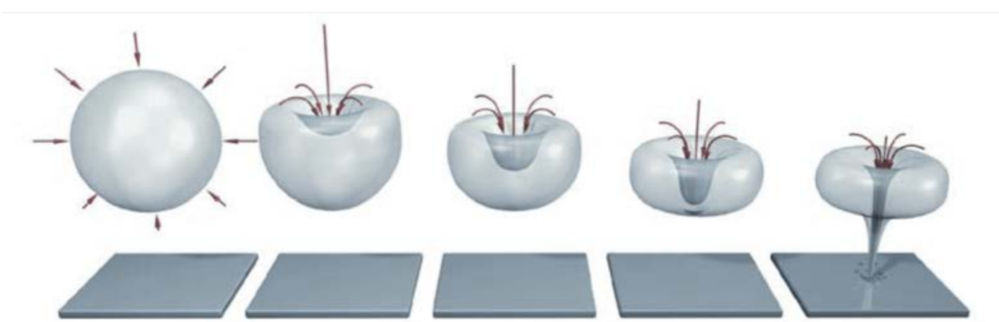


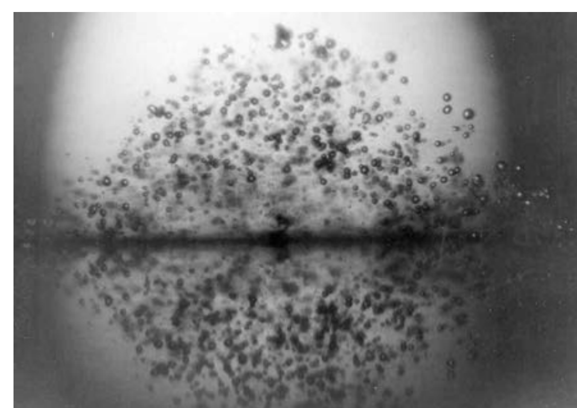
Generation of Micro Bubbles

Collapsing Bubble and its Effects

- Bubble volume pulsation around their equilibrium size can generate velocities that induce shear stresses on nearby
- Rapid collapse of bubbles generates momentary high temperatures in the bubble core. The hot bubble can induce chemical changes in the surrounding medium, including free-radical generation
- Asymmetric collapse (destruction) of the bubbles forms micro-jet.
- Growth and transient collapse of micro bubbles also causes formation of micro-turbulent eddies and shock waves.

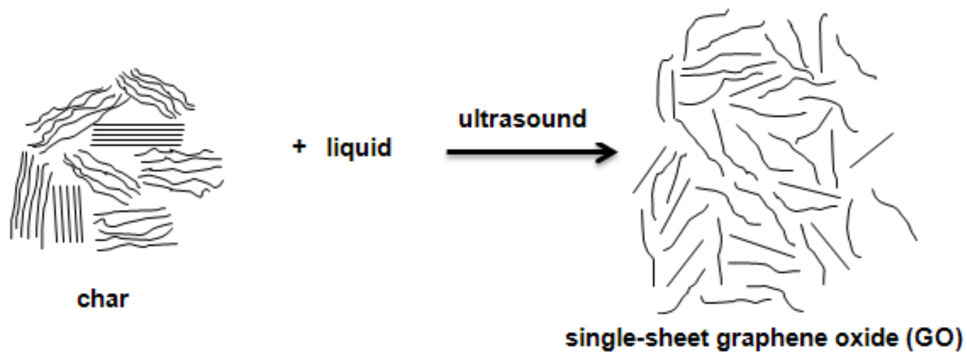






Ultrasound-Induced Exfoliation of Graphene and Graphene Oxide

Pioneering work of ultrasonic conversion of graphite oxide to graphene oxide: Stankovich, et al., Graphene-based composite materials. *Nature*. 2006, 442, 282-286.

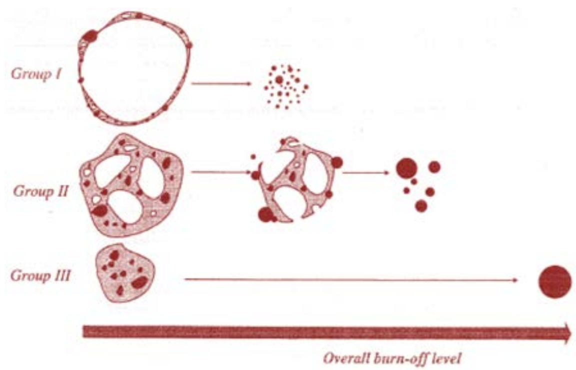


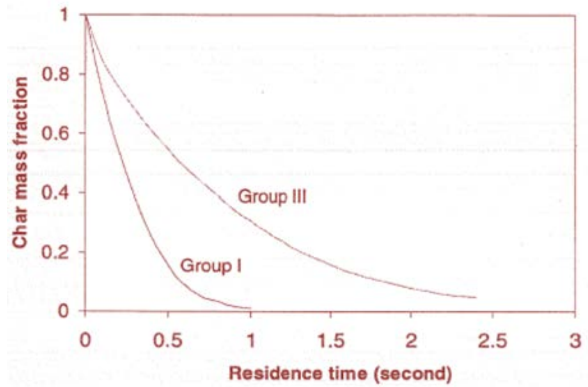
Our postulations:

- Ultrasound **exfoliates the graphitic and GO clusters** in chars into single-layered graphene and GO platelets, and therefore facilitates the reactivity of edge carbons of these platelets.
- It is also known that ultrasound **splits water**; the impacts of the hydrogen and hydroxyl radicals after water splitting on the char during treatment cannot be predicted.
- Ultrasound treatment removes minerals as **leaching minerals** from carbonaceous materials is a known technology.

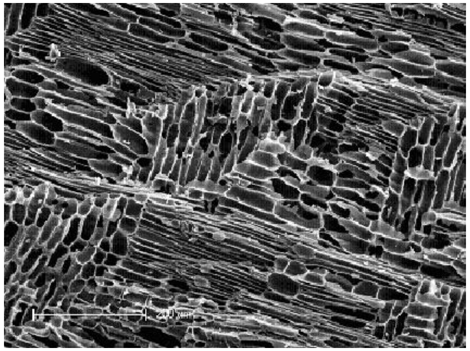
Concept 3: Coal Swelling by Polar Solvents

- Attacks of nucleophilic solvents breaks the hydrogen bonds, catalyzes the tautomerization, weakens cross covalent linkages in the carbon structure, and **swells the coal matrix**.
- Gasification of type I and type III particles (Wall et al., 2002):





<u>Our Postulations</u>:
Treatment of carbons with CO_2 and H_2O can
- swell the carbon,
- increase the internal surface area, and,
- increase the reactivity of carbon.



www.growingnewlife.com/index.php?p=1_12_Benefits-of-Biochar

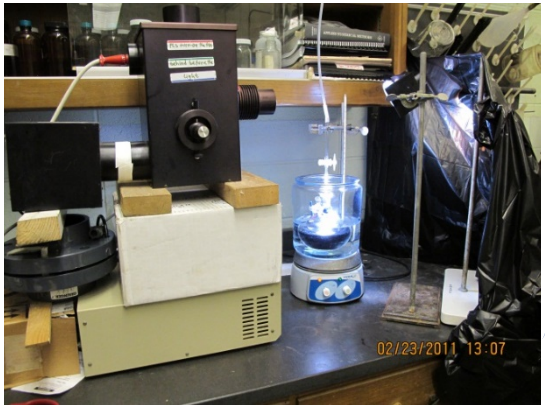
Enhancement of Biochar Quality and Functionalization of Biochar

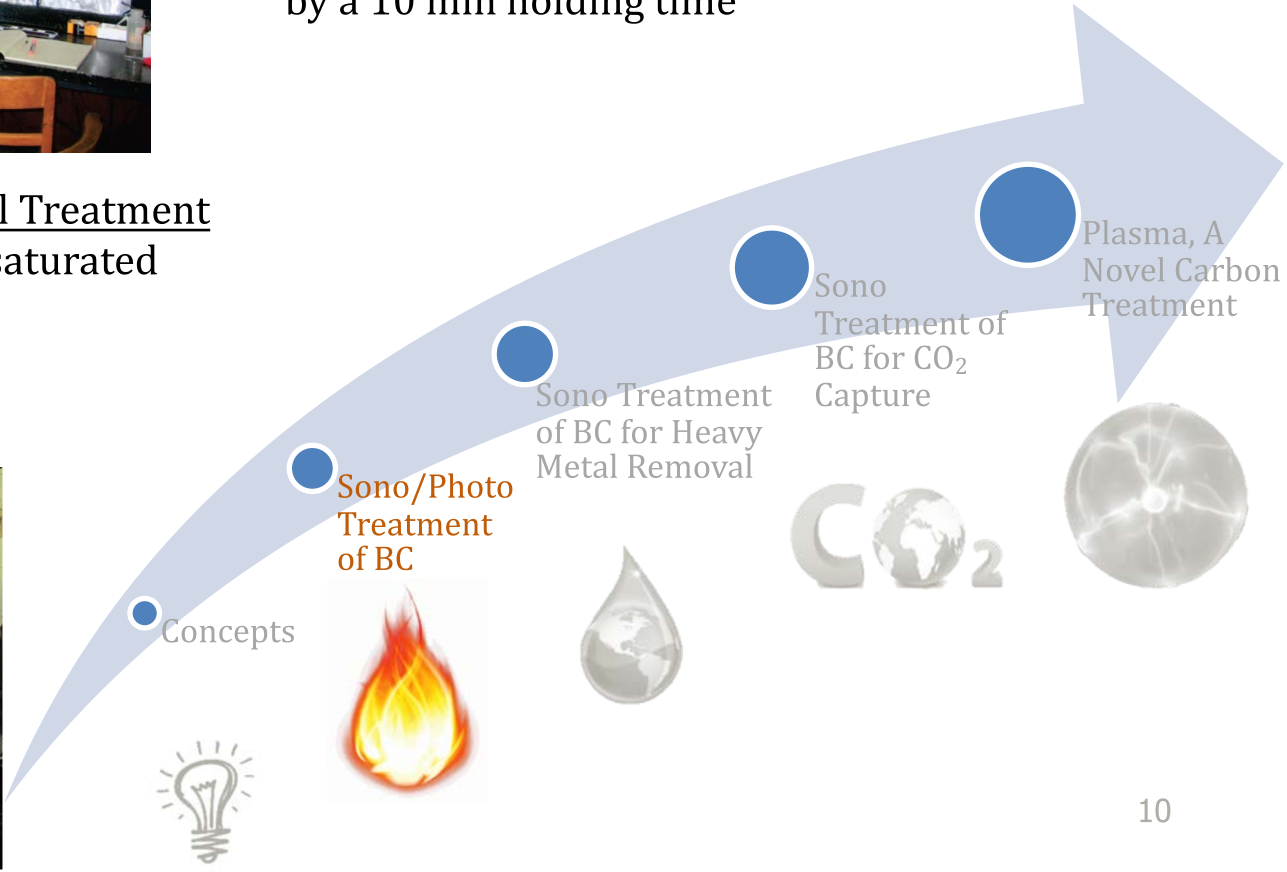
<u>Biochar Production</u>

- sorghum
- 75 and 106 μm
- heated in He with 5 ºC/min heating ramp to 550 ºC followed by a 10 min holding time

<u>Ultrasound and photochemical Treatment</u>

- 3 to 6 gm biochar + H_2O + saturated CO_2
- 65 ºC, 1 atm
- 3 min, 12 min, 5 h





Major Discoveries

A *single*-stage ultrasonic and/or photochemical treatment of biochar/H_2O/CO_2 systems leads to sizeable,

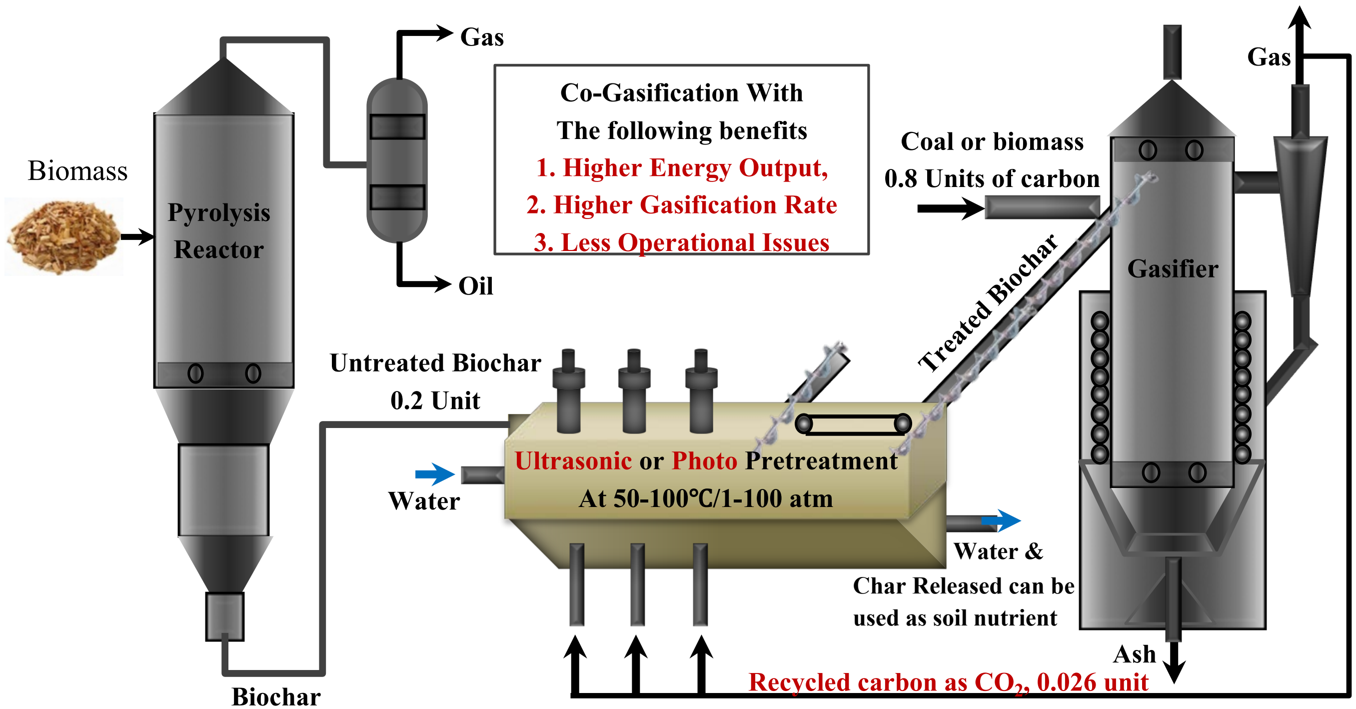
- **CO_2** (13%) and **hydrogen fixations** (24%) on carbonaceous substrates
- removals of **minerals** (K and Si, 60-97%) detrimental to combustion but beneficial to soil
- increase in **heating value** (HV) of the biochar (50%)
- increase in the **internal surface area** of the carbon materials (14 folds)

Scientific rationale and technological implications of these discoveries can be found in:

- Synergisms of Acoustic- and Light-Treatment of Biochar (e.g., *AIChE Journal*. 60(3), 1054-1065 (2014)

www.charcoalremedies.com/charcoaltimes/0512/biochar_revolution

The Pretreatment for a co-Gasification Process



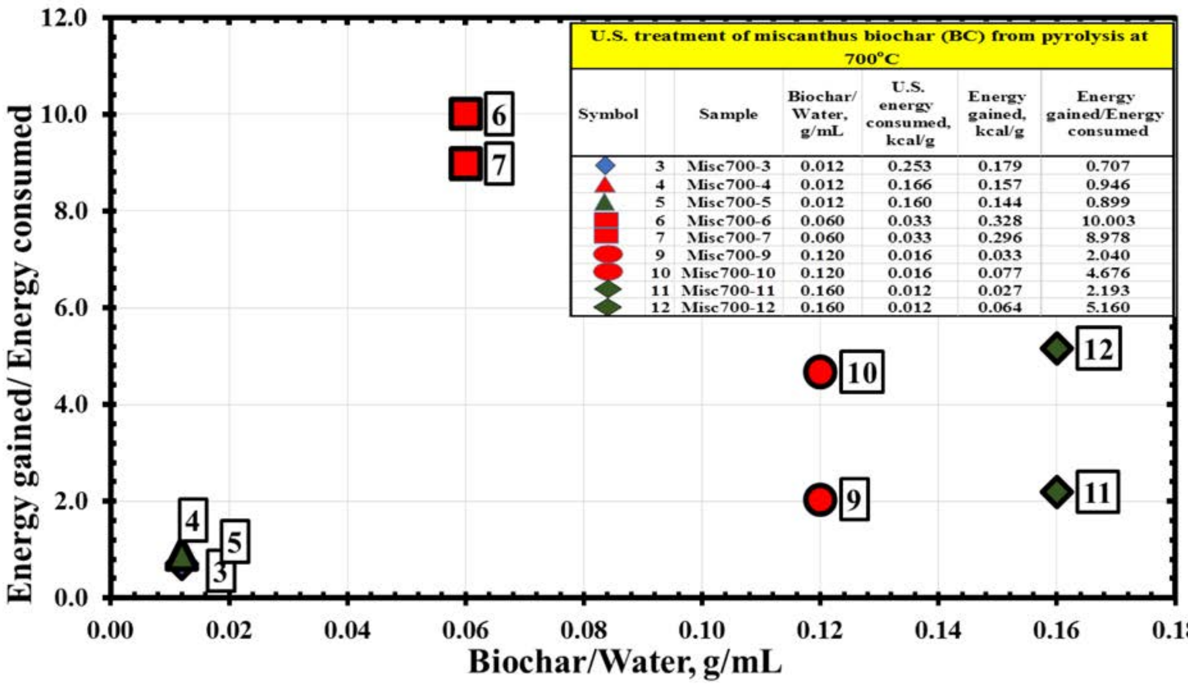
In a co-generation process where 20% of energy input comes from char, treatment results in

- Biochar's carbon content increases by 13%, implying 2.6% carbon recycle.
- Assuming char's heating value increases by 50% and 20% of such increase is used in the pretreatment process, the energy output from combustion of char will be 1.40 times of the raw char.
- For a *co-generation* power plant that uses only 20% char as fuel source, the overall energy output from char will increase to 28% (20% × 1.40), resulting in a net gain of 8% in the total output. This is not considered an incremental improvement for power plants.

Whether the acoustic energy is sufficiently low in achieving the goal?

Enhancement of Biochar Quality and Functionalization of Biochar

- Biomass origin, pyrolysis conditions and acoustic pretreatment conditions contain a complex network of variables.
- High alkalinity of carbon surface favors adsorption of protons and Lewis acids in aqueous solutions.
- Acidic organic functional groups, including carboxylic acids, lactones and phenols, are removed from BC surface during the heat treatment of biomass.



U.S. treatment of miscanthus biochar (BC) from pyrolysis at 700°C						
Symbol		Sample	Biochar/ Water, g/mL	U.S. energy consumed, kcal/g	Energy gained, kcal/g	Energy gained/Energy consumed
	3	Misc700-3	0.012	0.253	0.179	0.707
	4	Misc700-4	0.012	0.166	0.157	0.946
	5	Misc700-5	0.012	0.160	0.144	0.899
	6	Misc700-6	0.060	0.033	0.328	10.003
	7	Misc700-7	0.060	0.033	0.296	8.978
	9	Misc700-9	0.120	0.016	0.033	2.040
	10	Misc700-10	0.120	0.016	0.077	4.676
	11	Misc700-11	0.160	0.012	0.027	2.193
	12	Misc700-12	0.160	0.012	0.064	5.160

Acoustic- and Light-Enhanced Catalytic Conversion of CO_2

CH_2O participates in electrophilic aromatic substitution reactions with aromatic compounds resulting in hydroxymethylated derivatives:

$ArH + CH_2O \rightarrow ArCH_2OH$

Biochar has a stable carbon source and it contains TiO_2 that promotes photocatalytic reaction.

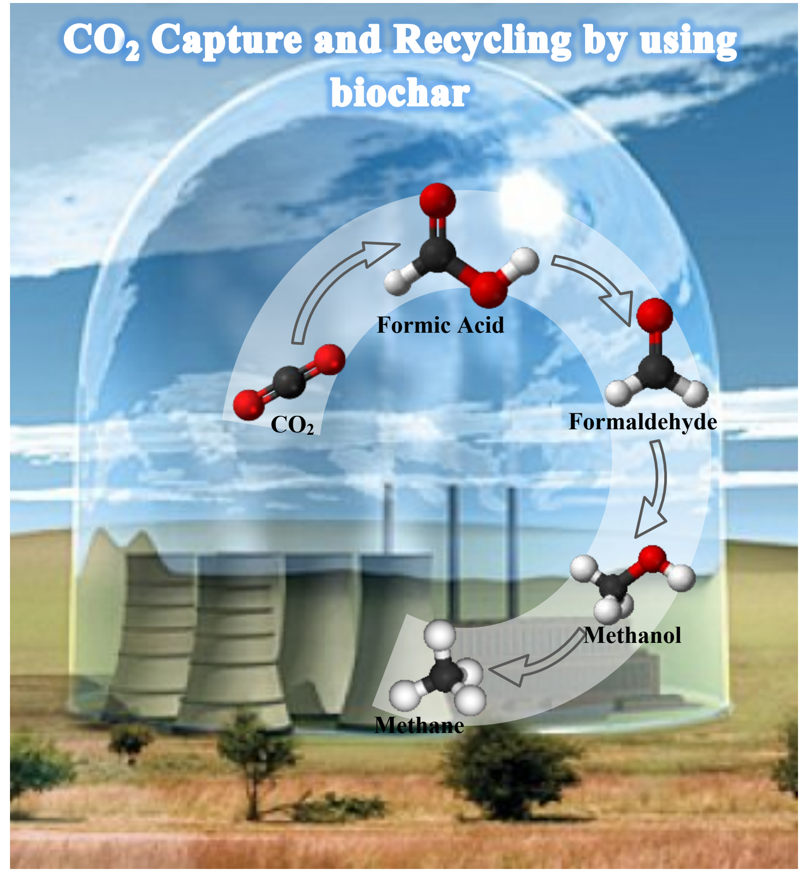


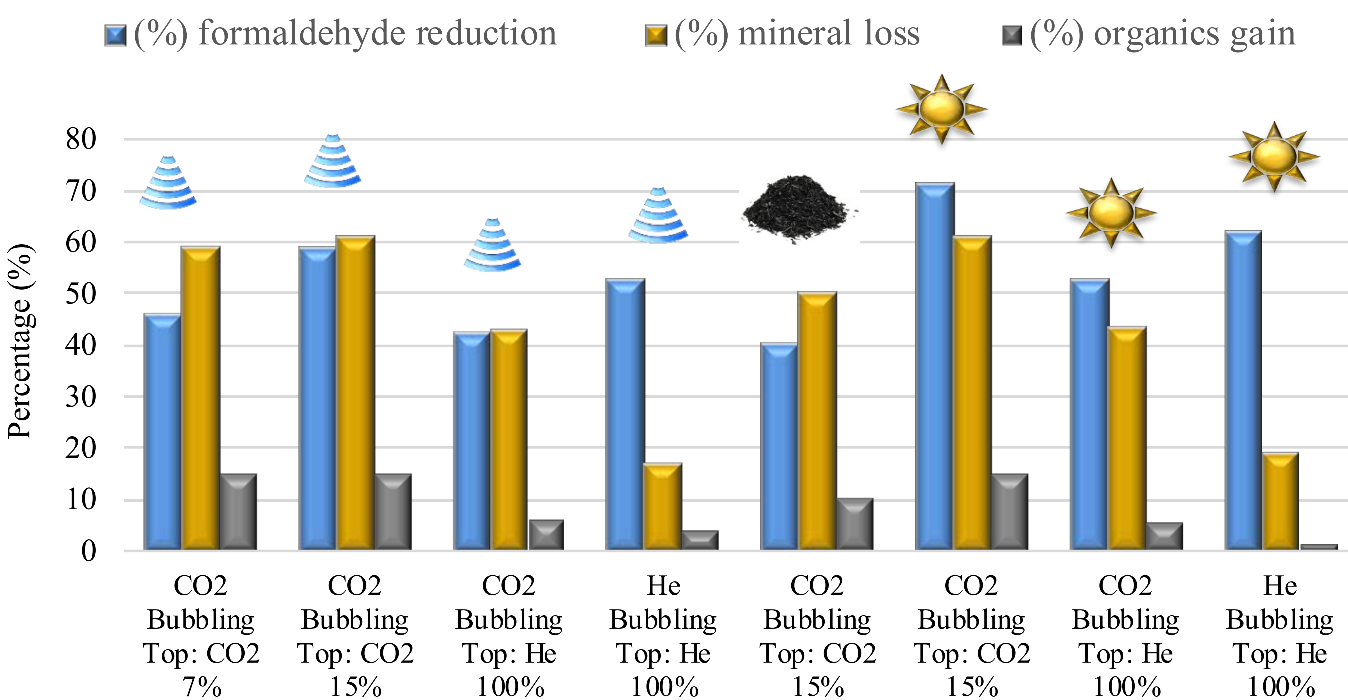
Figure 8: CO_2 Capture and recycling by using aromatic rings in biochar as a representative of the PAHs,●:Carbon,●: Oxygen,●: Hydrogen

Our postulations:

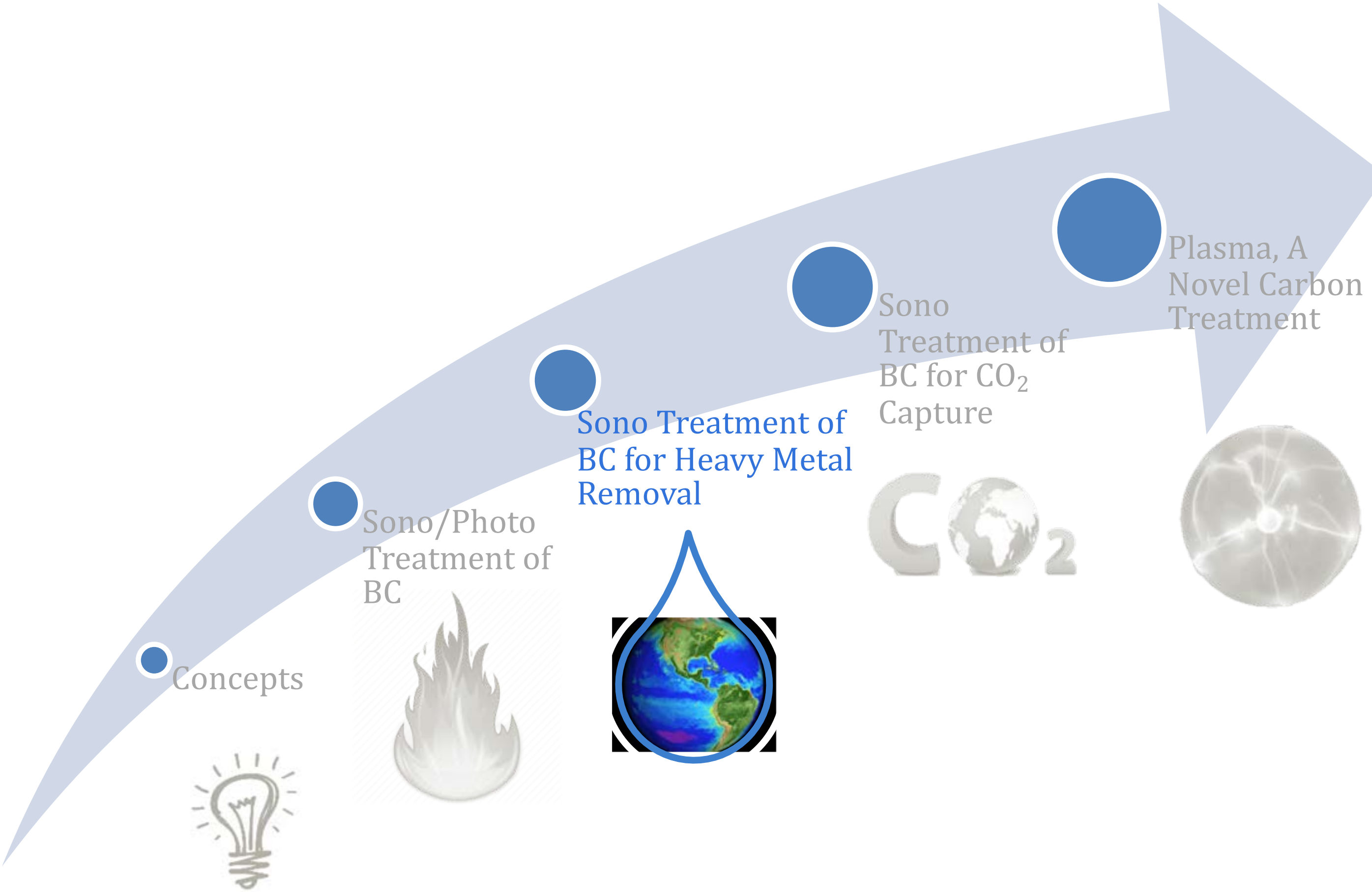
Fixation of carbon from CO_2 on biochar starts with formation of CH_2O followed by reactions between CH_2O and the aromatic structure in the biochar

Major Discoveries

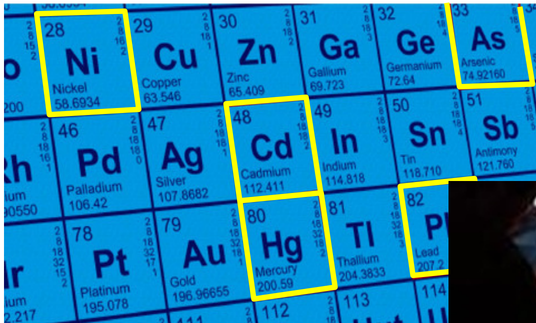
The ultrasound and photochemical treatments:
15 g of pinewood biochar, 250 ml water, saturated CO_2 or He
300 ppm HCHO, 0%, 7% or 15% CO_2 in the headspace
2000 J of ultrasonic or light energy



Ultrasono-Modification of Biochar for Heavy Metal Removal



Task 3, Project 6 : Sources of Heavy Metal Pollutants



Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters

The toxic metals in wastewater sometimes reach to the high concentrations 500 mg/L

Pollutants	Potential Health Effects
Cadmium	Kidney damage
Arsenic	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer
Lead	Kidney problems; high blood pressure
Mercury	Kidney damage
Chromium	Allergic dermatitis
Copper	Long-term exposure: Liver or kidney damage
Nickel	Long-term exposure: lung cancer, prostate cancer, larynx cancer, heart disorders, chronic bronchitis, and asthma

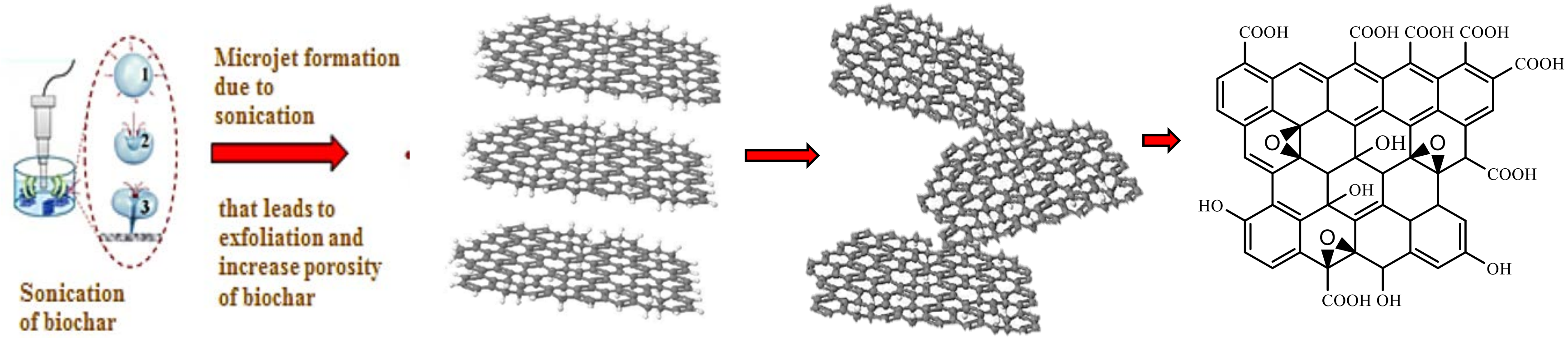
Source: National Primary Drinking Water Regulations

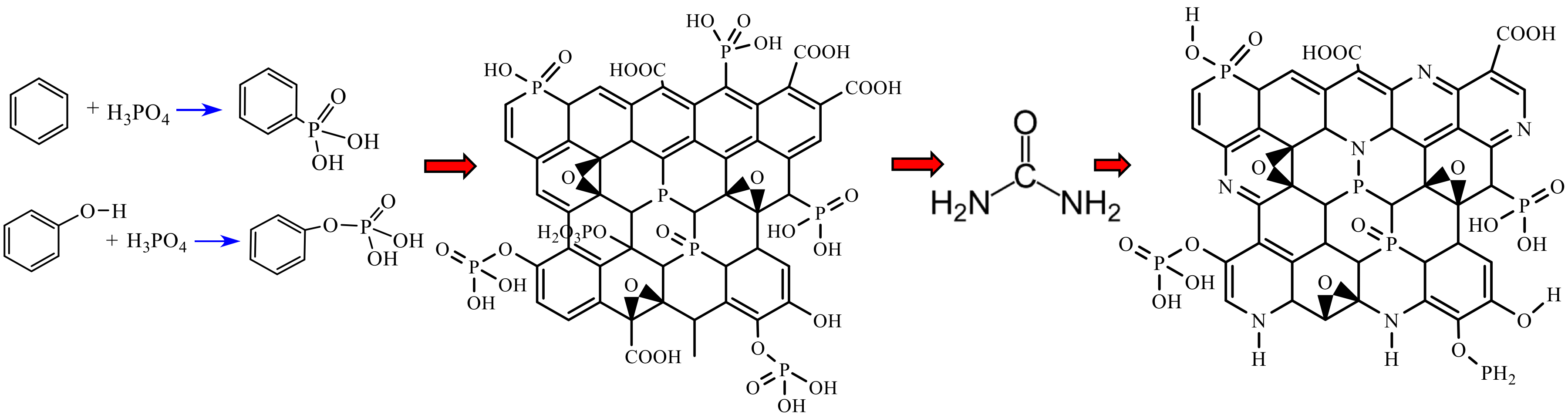
RIVER OF BLOOD:

Arctic river turns RED after nickel processing plant LEAKS into waters

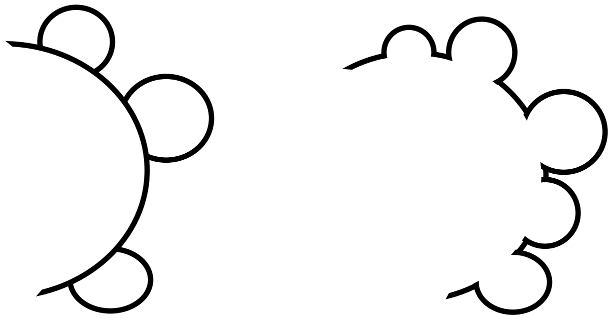
14 June 2018

The Mechanism involving sonication, phosphoric acid treatment and urea functionalization of biochar



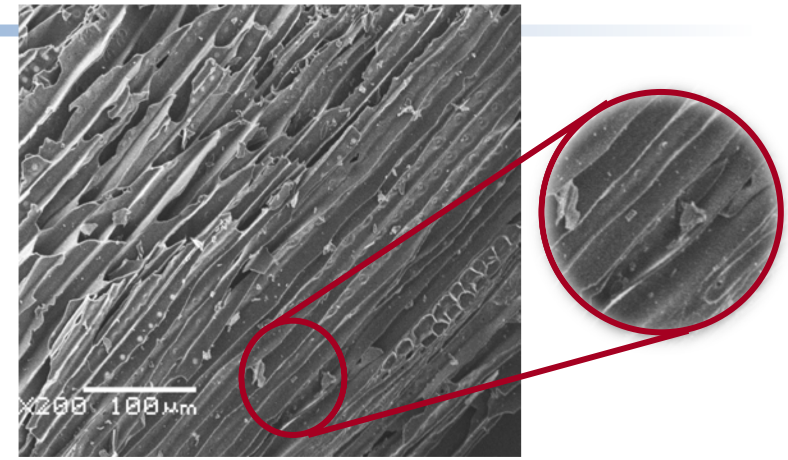


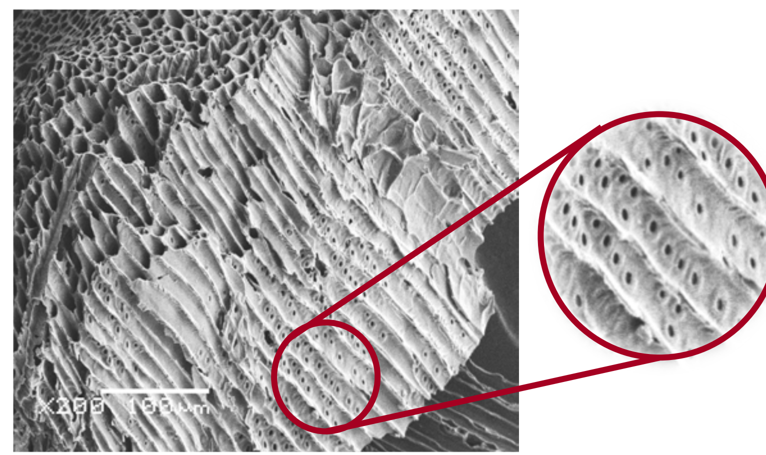
Results and Discussion

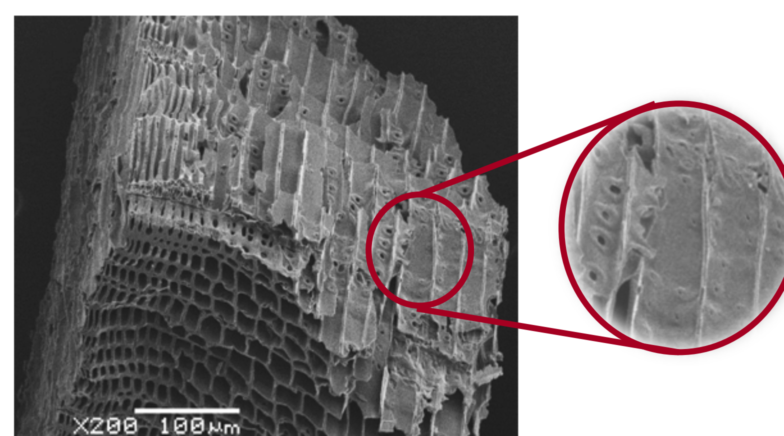


When biochar is exposed to cavitation induced by ultrasound, the generation of new micropores, or the opening of blocked ones, increases its microporosity and reduces its macro- and mesoporosity.

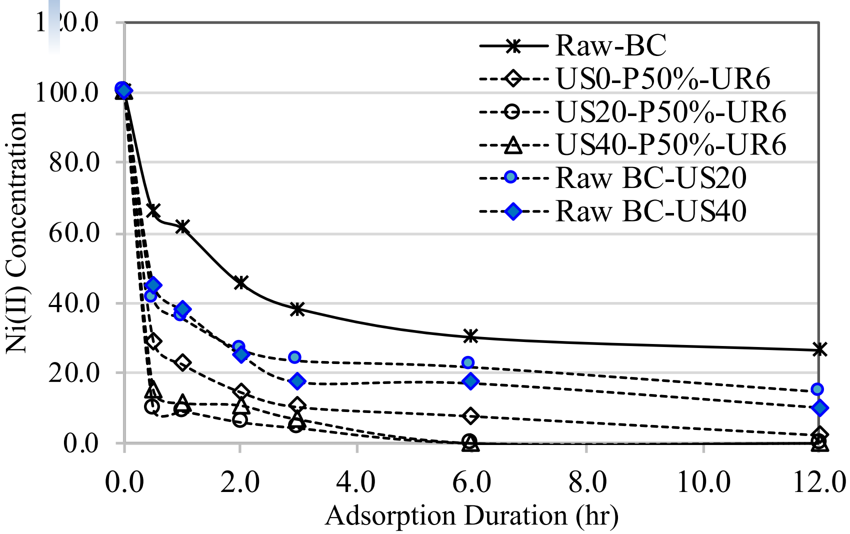
Micro and Macro porosity of Raw and Ultrasono-Modified Biochar				
	Micro-Porosity		Macro & Meso Porosity	
Sonication Time (s)	DR Surface Area (m^2/g)	Porosity (cc/g)	BET Surface Area (m^2/g)	Porosity (cc/g)
0	347.024	0.096	69.055	0.050
20	389.608	0.108	54.074	0.042
40	383.530	0.128	34.304	0.028
60	392.937	0.131	26.641	0.023





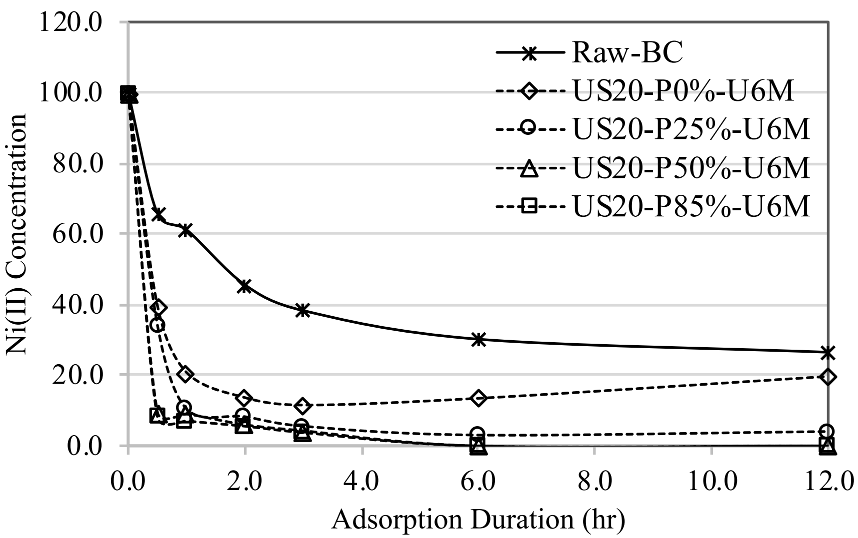


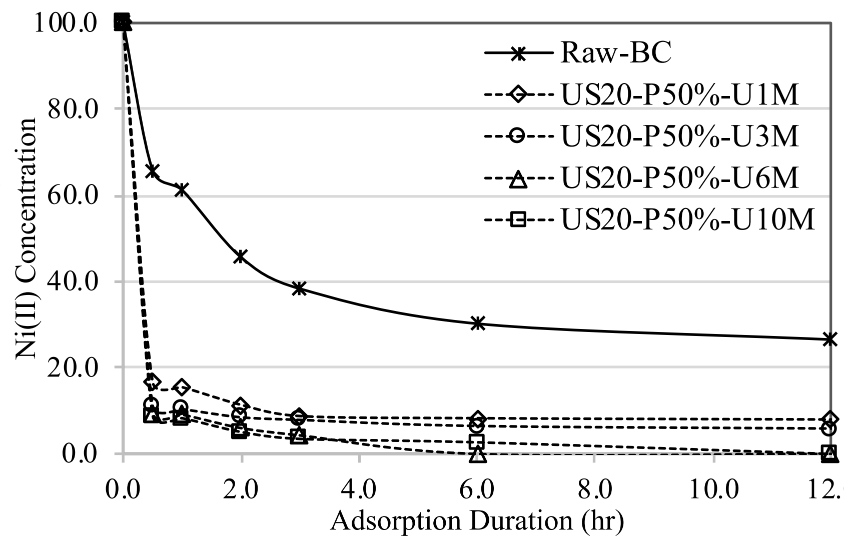
Task 3: Results and Discussion



Expectedly, ultrasound irradiation significantly increased the adsorption capacity of biochar thorough changes in biochar structure, but it still could not remove Ni(II) completely after 12 hours.

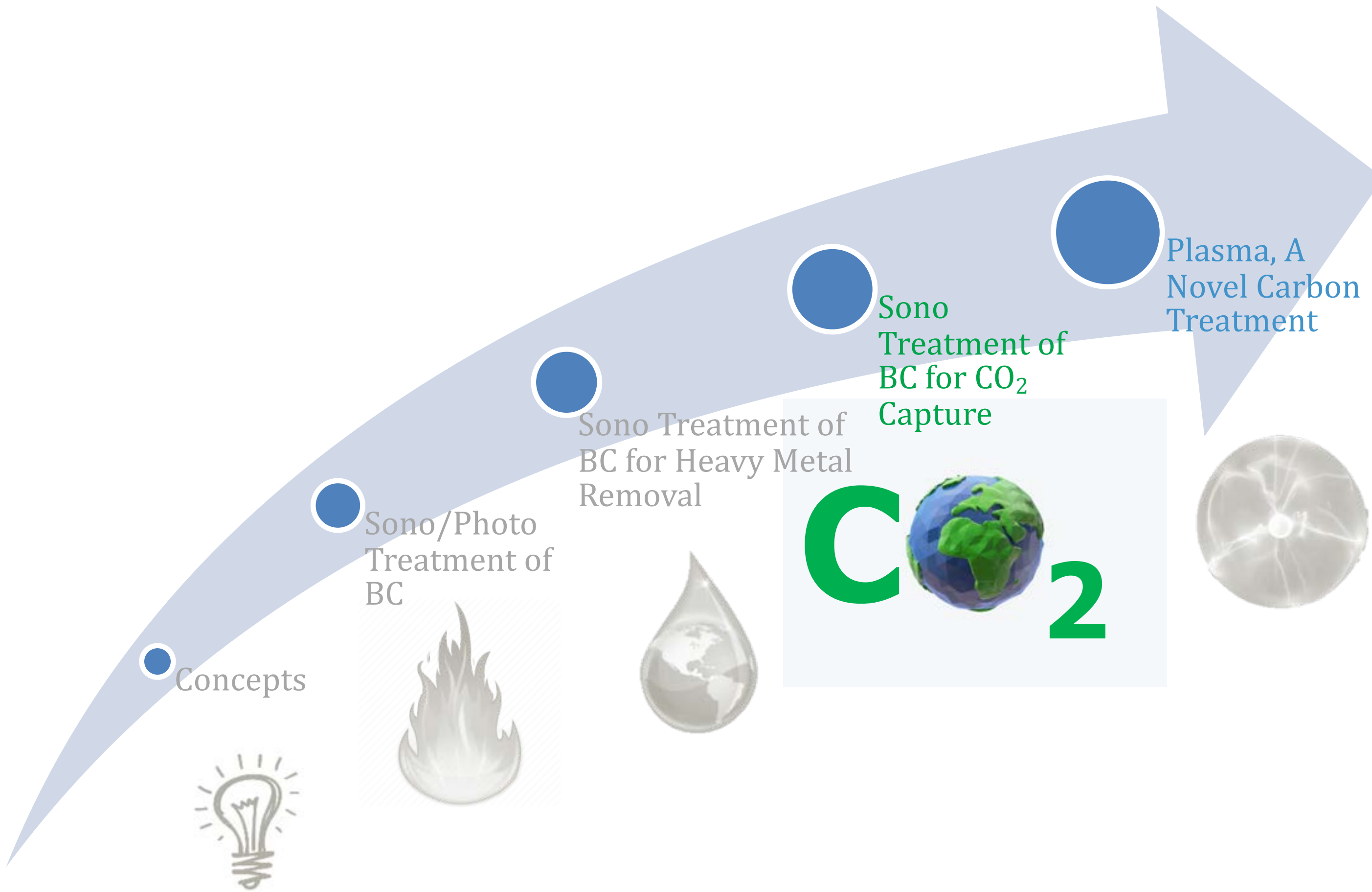
Biochar modified with 1M or 3M urea seemed to saturate their adsorption ability after 3 hours, at about 90%.



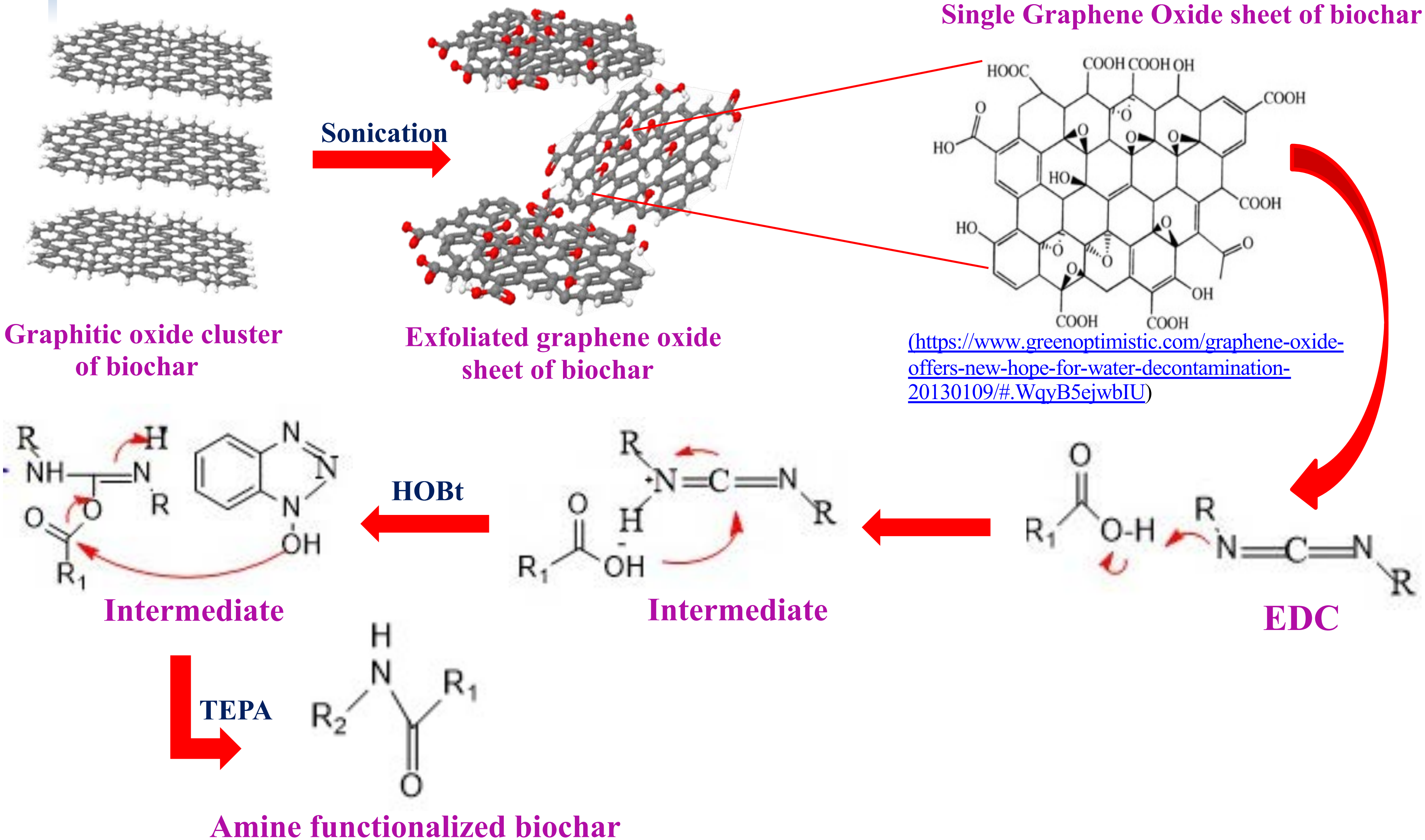


Treatment even without phosphoric acid gave a biochar that adsorbed Ni(II) much better than raw biochar. However, a sign of leaching was observed in longer durations.

Ultrasono-Modification of Biochar for CO_2 Capture



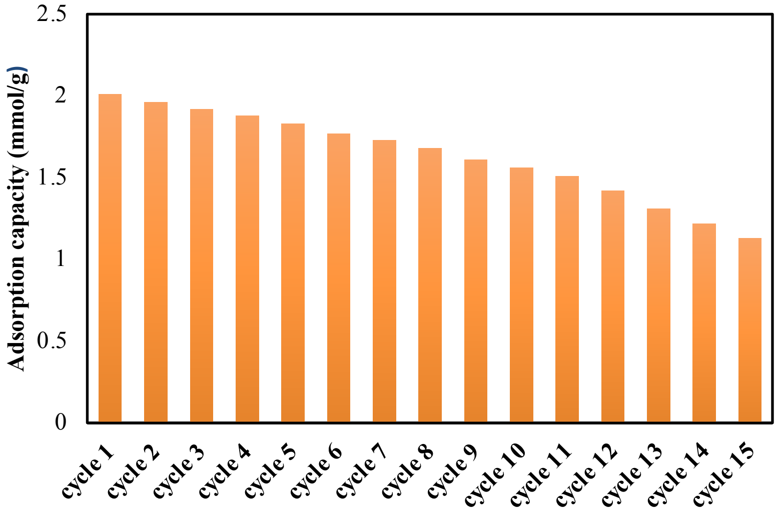
Amine functionalized P&UCEB for CO_2 capture, Mechanism Of Biochar Activation



- **Functional groups of biochar (-COOH, -OH, C=O)**

Amine functionalized P&UCEB for CO_2 capture

Sample Name	Adsorption capacity (mmol/g)	Temp. (°C)	CO_2 Conc. (vol %)
Raw Biochar	0.3	70	10
Low power US	**Effect of ultrasonic power**		
US0-EH1:1-T2.5	0.56	70	10
US0.5-EH1:1-T2.5	1.69	70	10
US1-EH1:1-T2.5	0.78	70	10
US3-EH1:1-T2.5	0.69	70	10
High power US	**Effect of ultrasonic power**		
US0-EH1:1-T2.5	0.55	70	10
US0.5-EH1:1-T2.5	2.04	70	10
US1-EH1:1-T2.5	1.73	70	10
US3-EH1:1-T2.5	1.58	70	10
High power US	**Effect of CO_2 concentration (vol%)**		
US0.5-EH1:1-T2.5	2.04	70	10
US0.5-EH1:1-T2.5	2.31	70	13
US0.5-EH1:1-T2.5	**2.79**	**70**	**15**

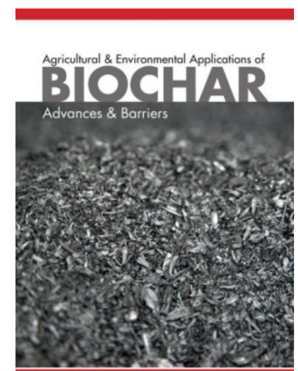


- **Conditions:** Temperature - 180° C
  Duration -1 hour
  Helium gas flow rate – 500 cc/min
- After 15 cycles the ultra-sonicated amine functionalized biochar retained it's 56% initial adsorptive capacity

Sustainable Energy & Environment Group

- **Over 250 participants around the world for the activities described below**
- **New courses on alternative energy and environment in the US and abroad**
- ***Handbook of Climate Change Mitigation and Adaptation,* 4 volumes, 3331 pages, Springer, 2012 and 2017, http://www.springer.com/us/book/9783319144085#otherversion=9783319144092**
- **International workshops, short courses, outreach to K12 students & citizens**

Writing & releasing a Book
With particular focus on biochar's
Synthesis, Modification, Application

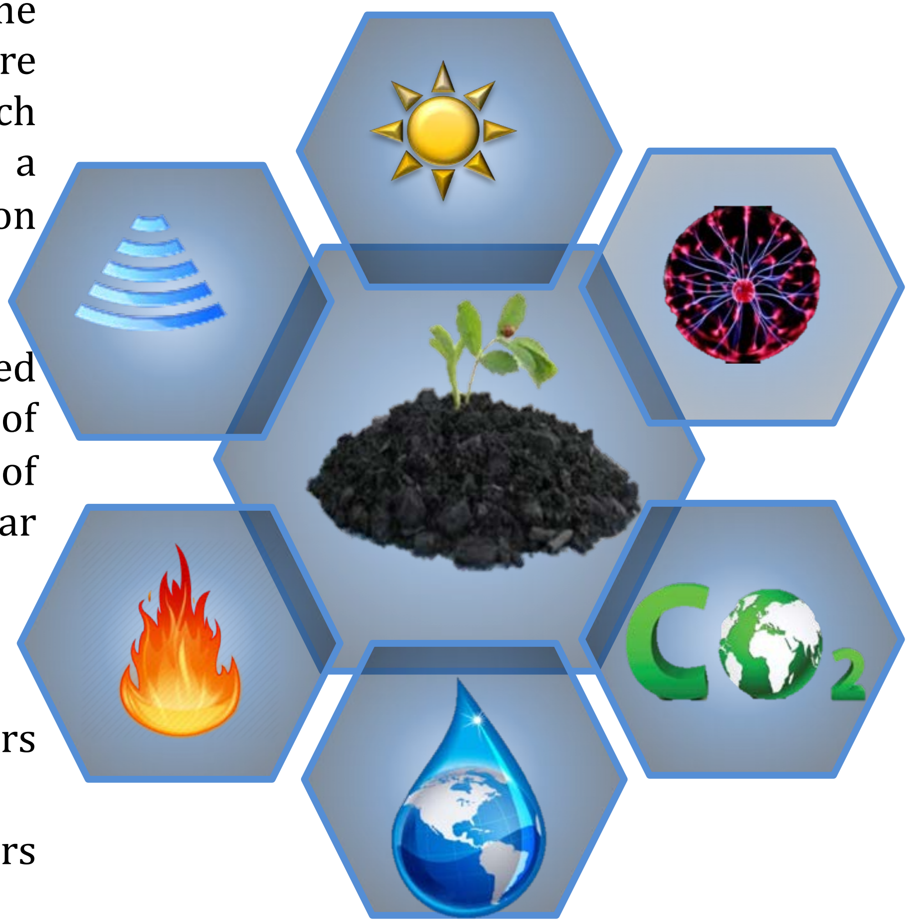


frontiers in Energy Research

Conclusion

- Contrarily to traditional carbon activation at high temperatures (>600C), all stages of the ultrasono/Photo/chemical activation are conducted at low temperatures which demonstrate that this type pf activation is a feasible strategy for enhancing the adsorption capacity of biochar.

- Although, ultrasound/Photo assisted Modification/activation/functionalization of biochar appears promising, but the effects of parameters have to be investigated in the near future.



Future Applications

- Sono/photo/plasma-Functionalized Biochars for Supercapacitor
- Sono/photo/plasma-Functionalized Biochars for Remediation of Oil Spill
- Sono/photo/plasma-Functionalized Biochars for Water Treatment

Thank You.

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https://engineering.olemiss.edu/seeg/