Nitrate Retention and Release by Biochars Produced from Fast Pyrolysis

(R. Chintala et al., Micropor Mesopor Mat, 2013)

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Rationale/Background

- Biochar is a by-product generated during pyrolysis of biomass feedstocks to create energy products
- Biochar – as a soil amendment, exhibit strong affinity for anionic agricultural nutrients and influence their bioavailability
- Nitrification – quickest reaction pathway, highly mobile nitrate ion
- Study to determine the retention and release of nutrients by biochars and its underlying mechanism

Objectives

1. Quantify the potential of non-activated biochars and activated biochars to sorb nitrate ion

2. Study the desorption kinetics of nitrate by non-activated biochars and activated biochars

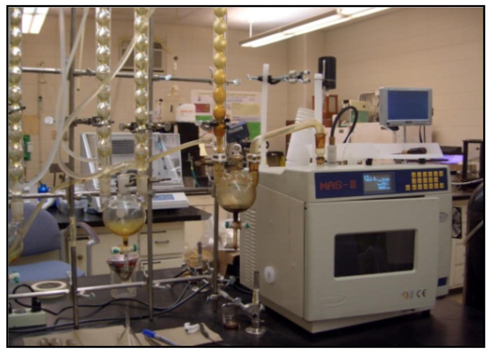
Feedstocks & Pyrolysis

Corn stover (*Zea mays L*)

Switchgrass (*Panicum virgatum L*)

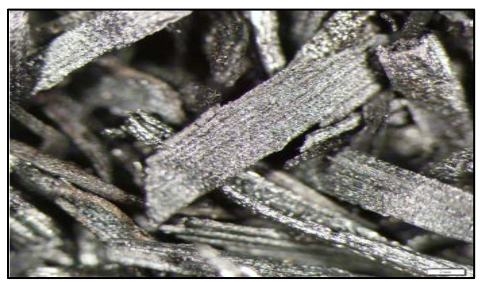
Ponderosa pine wood residue (*Pinus ponderosa Lawson and C. Lawson*)

Microwave pyrolysis



- Temperature – 650 ^{0}C
  Residence time – 18 min
  Power – 700 w

Corn stover biochar



Switchgrass biochar

Ponderosa pine wood residue

Feedstocks & Pyrolysis

Production of non-activated and activated biochars

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Biochar surface characterization

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Nitrate sorption by non-activated and activated biochars

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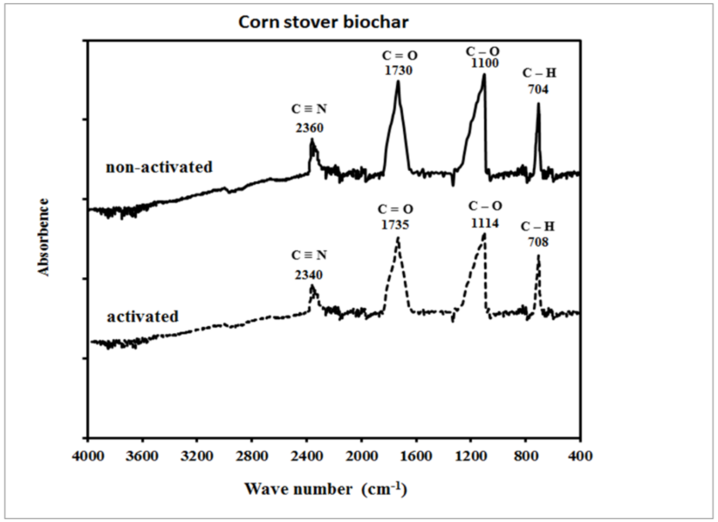
Nitrate desorption by non-activated and activated biochars

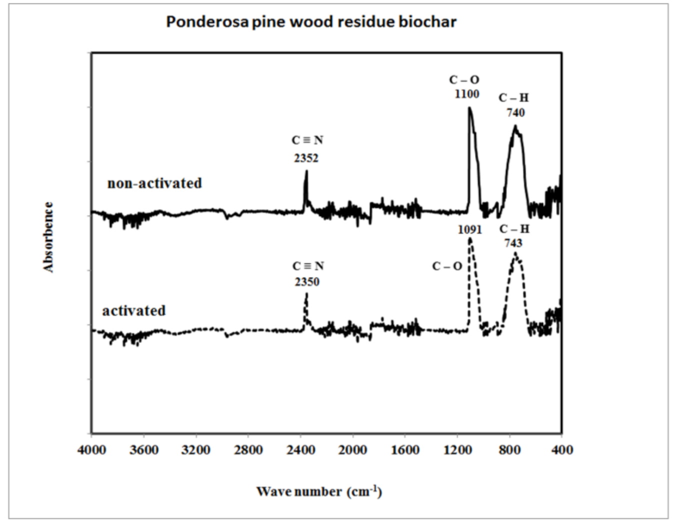
Biochar Characterization

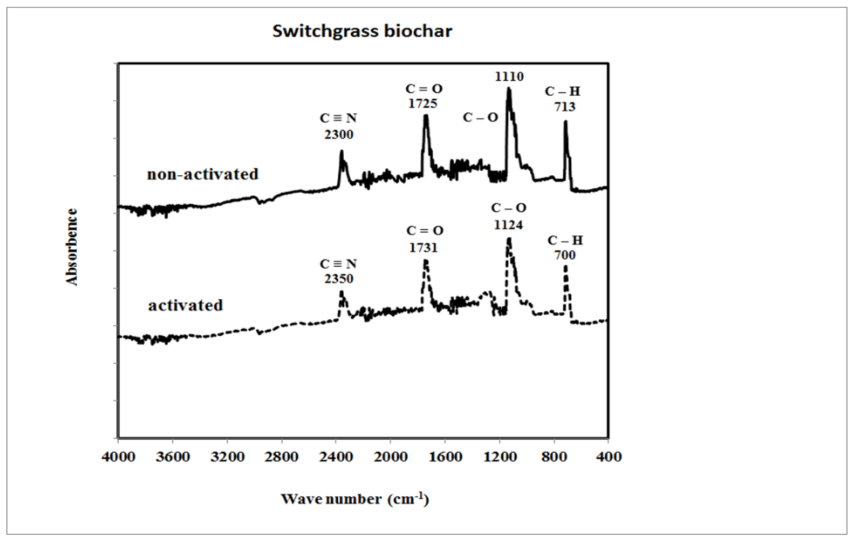
Properties	CSB		PWRB		SGB	
	Non-activated	activated	Non-activated	activated	Non-activated	activated
Specific surface area (m^2g^{-1})	43.4±2.5	513±21	52.1±4.1	456±15	48.0±2.6	582±23
pH	10.5±0.04	8.16±0.10	7.85±0.02	7.05±0.11	9.73±0.24	7.75±0.10
EC(μS cm^{-1})	3000±61	140±21	200±22	110±15	890±21	152±16
CEC ($Cmol_c$ kg^{-1})	41.6±5	134±11	32.5±3	115±7	43.1±2	149±8
PZNC	6.67±0.15	4.63±0.13	5.75±0.03	3.04±0.07	7.08±0.44	4.92±0.14
VOC (g kg^{-1})	206±21	58.5±8	125±11	45.1±6	184±15	59.1±7
Total N (g kg^{-1})	13.5±0.3	12.8±0.1	4.82±0.1	4.94±0.03	15.8±0.7	15.2±0.5
Total C (g kg^{-1})	742±10	726±13	845±30	801±14	763±22	720±17

*CSB = Corn stover biochar, PWRB = Ponderosa pine wood residue biochar, SGB = Switchgrass biochar

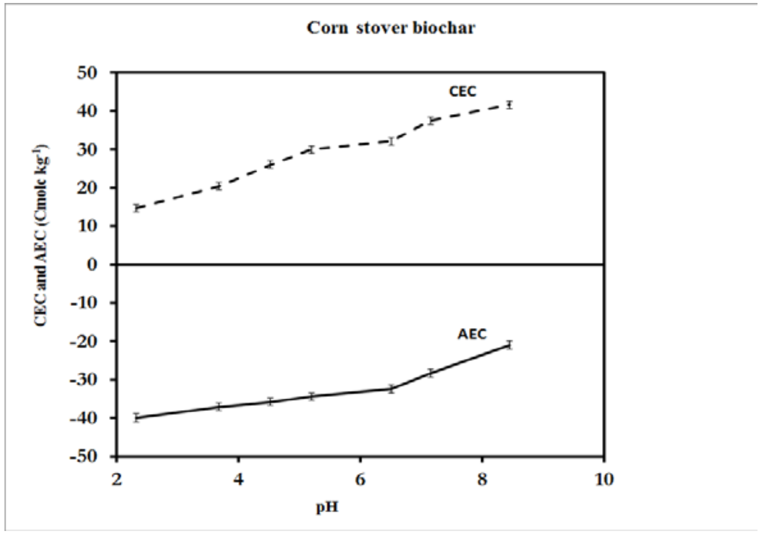
FTIR-Spectra

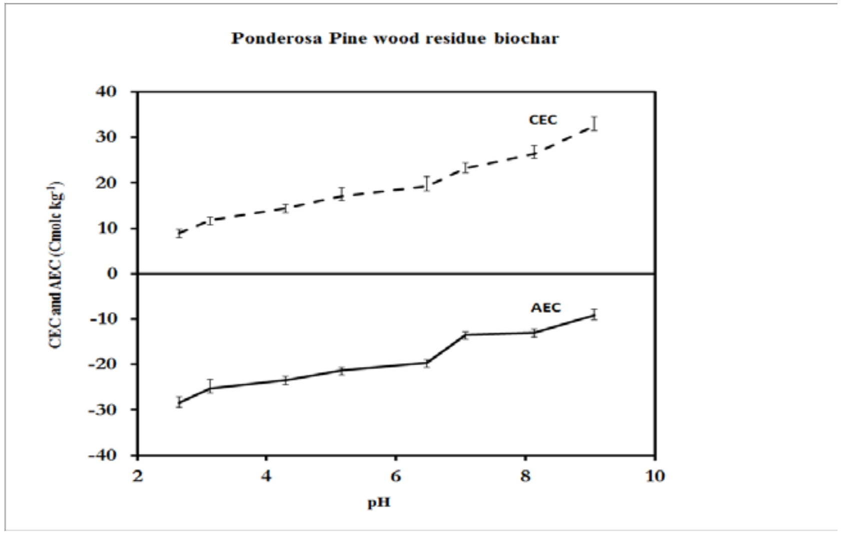


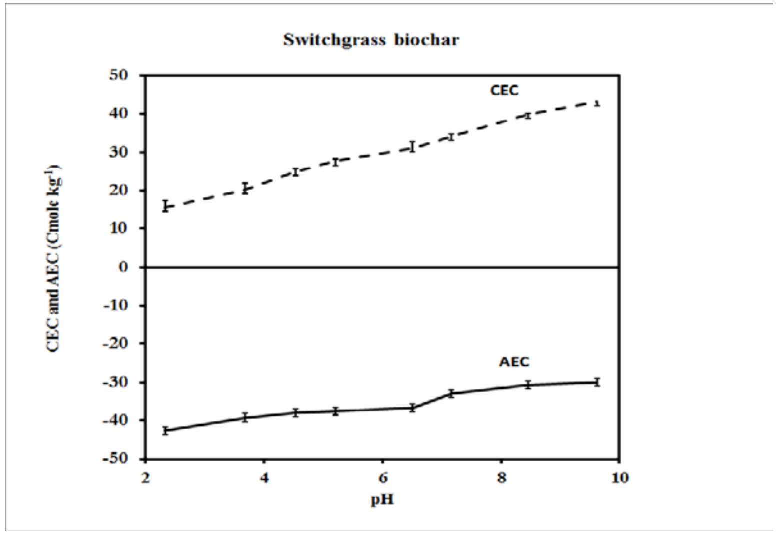




Surface Charge vs pH







- **CEC – switchgrass biochar (43.1±2) > corn stover biochar (41.6±5)> Ponderosa pine wood residue biochar (32.5±3)**
- **AEC – switchgrass biochar (42.7±3.66)> corn stover biochar (40±2.45)> Ponderosa pine wood residue biochar (29.8±2.12)**
- **PZNC – switchgrass biochar (7.08±0.44) > corn stover biochar (6.67±0.15)> Ponderosa pine wood residue biochar (5.75±0.03)**
- **VOC (%) – corn stover biochar (20.6) > switchgrass biochar (18.4) > Ponderosa pine wood residue biochar (12.5)**

Batch Experiment

Nitrate sorption isotherms:

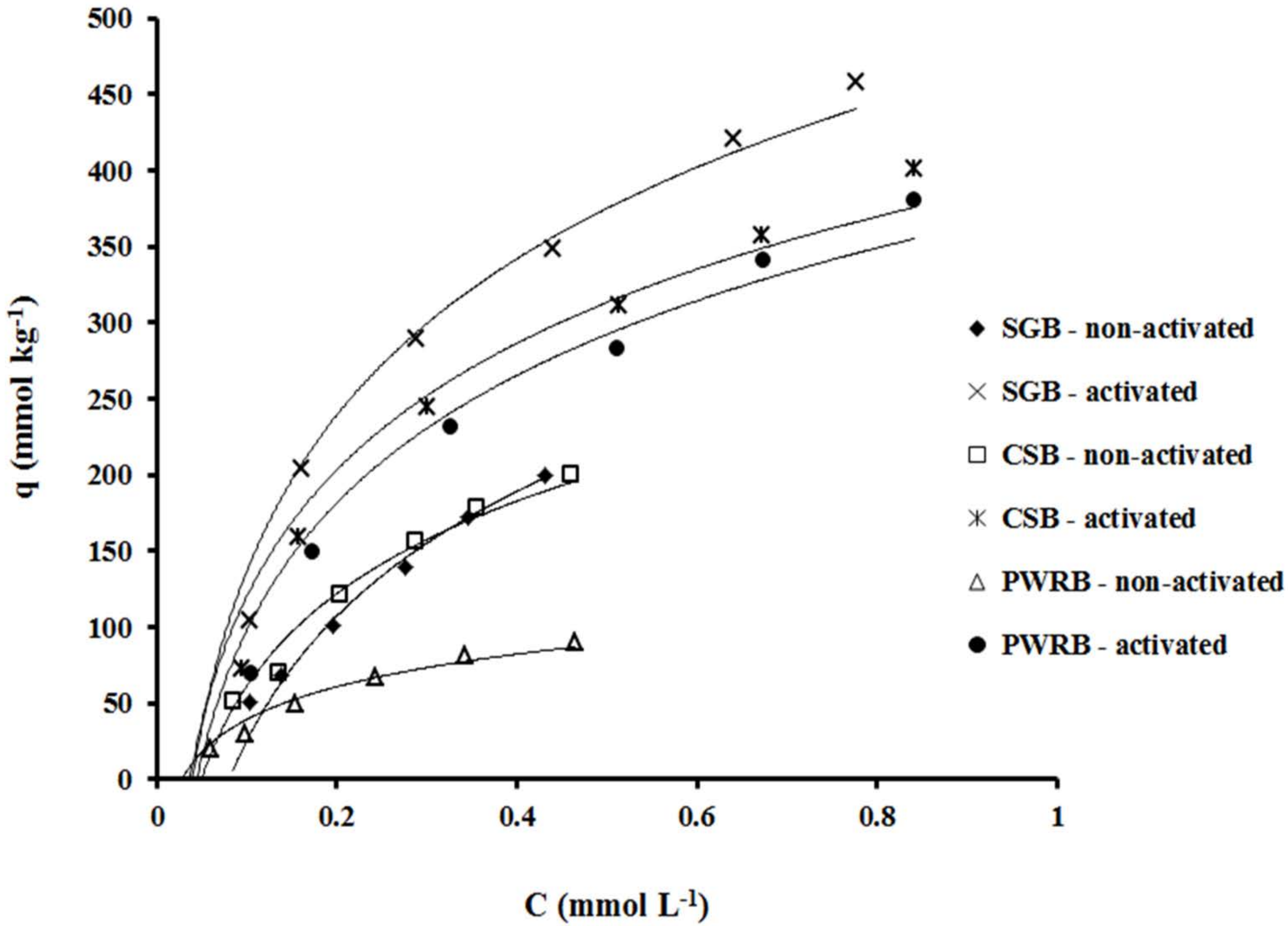
- **Initial nitrate concentration of solutions: 0, 0.16, 0.32, 0.64, 1.29, and 1.61mmol L^{-1}**
- **Shaking – 24 hr, 250 rpm, temperature 24 ^{0}C**
- **Isotherms: Freundlich equation** $q = K_f\, c^{1/n}$
  Langmuir equation $q = K_L bc/ (1+K_L c)$

  Where q = sorbed P (mg kg^{-1} of P), c = P concentration in the equilibrium solution (mmol L^{-1}), K_f = Freundlich partitioning coefficient, 1/n = sorption intensity, b = adsorption maxima (mmol kg^{-1} of P), and K_L = parameter related to binding energy (L kg^{-1}).

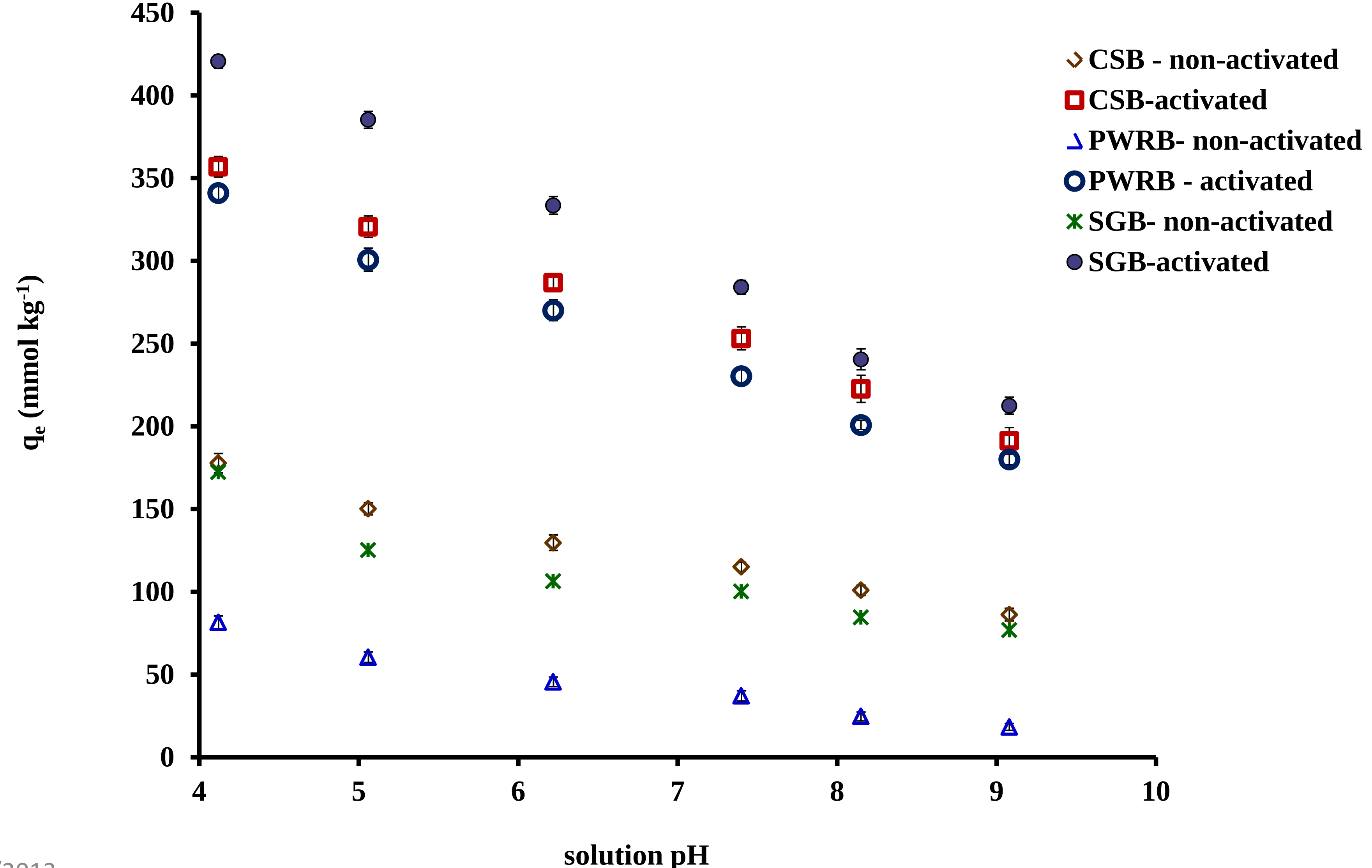
Desorption of Nitrate:

- **Initial nitrate concentration of solutions: 0.16, 0.64, 1.29 mmol L^{-1}, deionized water at pH 4.0 and 9.0**
- **Desorption (%) = (desorbed nitrate / adsorbed nitrate) *100**
- **Desorption kinetics - $\ln (P_0 - P_t) = a - K_d .\, t$**
  Where P_t = desorbed nitrate at time t (mmol kg^{-1}), P_0 = desorbed nitrate at equilibrium (mmol kg^{-1}), K_d = kinetic constant (h^{-1}), t = time (min), and a = constant.

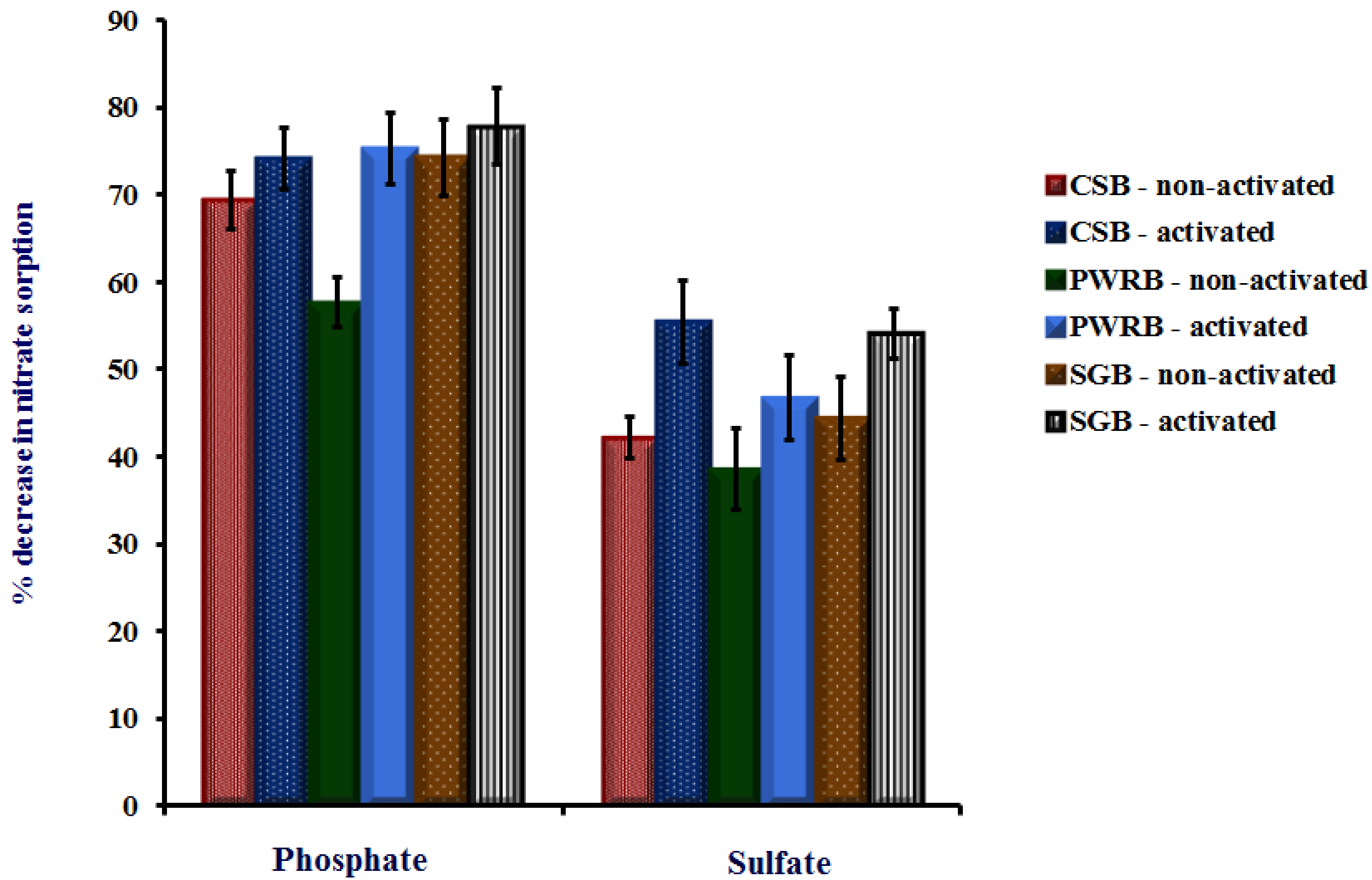
Nitrate Sorption Isotherms



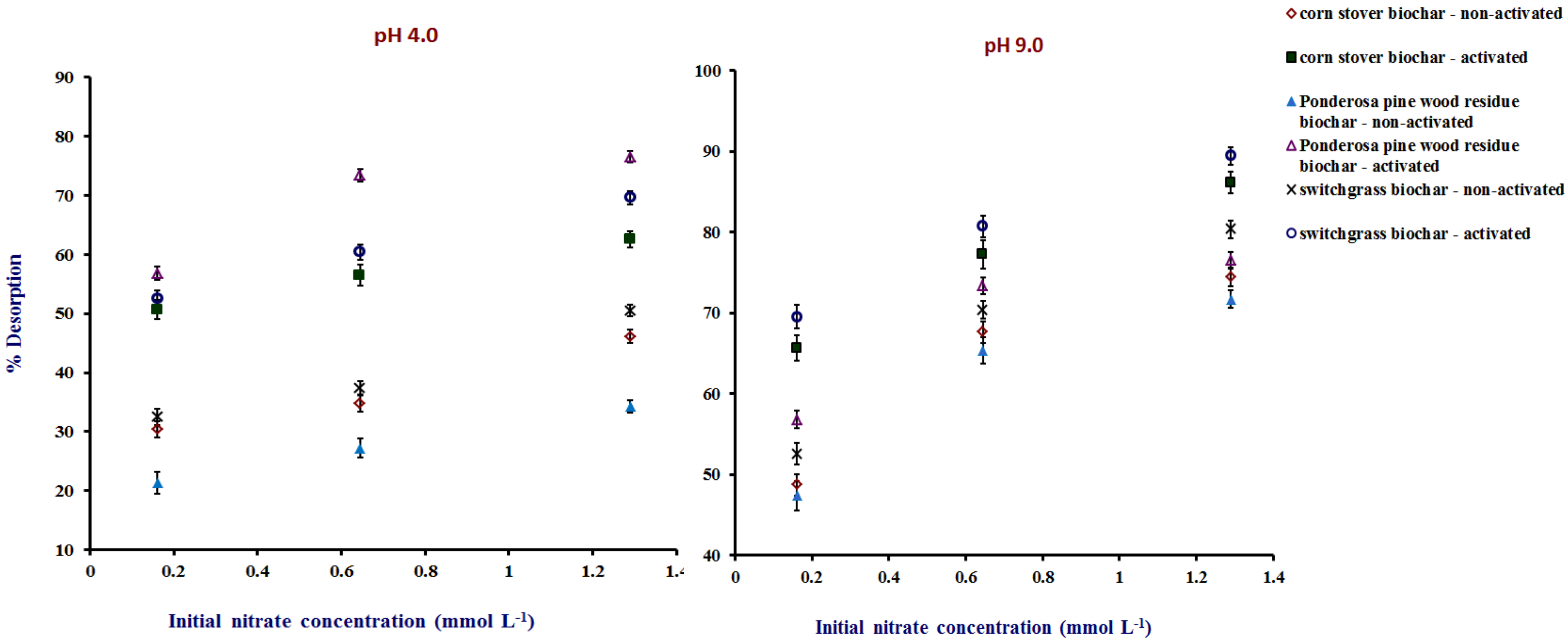
Nitrate Sorption vs pH



Nitrate vs Multivalent Anions



Nitrate Desorption vs pH



Nitrate Desorption Kinetics

Biochar type	a	$K_d \times 10^2$	SE	R^2
CSB – non-activated	4.35	2.78	0.05	0.97
CSB – activated	5.05	2.81	0.08	0.99
PWRB – non-activated	3.61	3.48	0.07	0.95
PWRB –activated	5.09	3.52	0.05	0.97
SGB – non-activated	4.38	2.79	0.03	0.96
SGB – activated	5.33	2.83	0.09	0.98

Conclusions

- The nitrate sorption capacity of biochars was observed to depend on surface properties of biochar (surface area and surface charge), solution pH, and presence of competitive ions with high negative potential.
- In higher nitrate concentration systems, the activated biochars have greater utility in reducing the availability of nitrate ions for biological de-nitrification and also mitigating the eutrophication.
- Biochars may also increase the residence time of highly mobile nitrate ions and make them more available for plant and nutrient utilization under conditions of limited N availability.
- Nitrate desorption was higher for chemically-activated biochars and increased solution pH.