BIOCHAR MODIFICATION WITH HEMATITE AND GOETHITE FOR EFFICIENT ACTIVATION OF PERSULFATE

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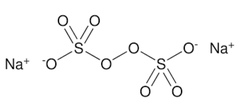
Introduction

In recent years, persulfate based Advanced oxidation processes (AOPs) are widely used in degradation of contaminants. Activated persulfate has high oxidation potential to degrade contaminants (Kolthoff and Miller, 1951). Biochar is emerging as sustainable and low cost alternatives of persulfate activation. However, biochar alone is inefficient in persulfate activation. Iron and its oxides are found to be efficient in persulfate activation (Rastogi et al., 2009). This study is conducted to modify biochar through pyrolysis of pretreated pine needle with natural Hematite or Goethite to incorporate iron oxide in the form of γ-Fe2O3 . Thermal treatment changes the forms of iron oxide α-FeO(OH) or α-Fe2O3 that is present in natural mineral into γ-Fe2O3 which have strong magnetic property. Magnetic biochar have higher sorption and activation removal ability towards contaminants and could be the effective strategy for the recovery of catalyst.



$S_2O_8^{2-} + e^- \rightarrow SO_4^- + SO_4^{2}$

Fig 1. Persulfate activation

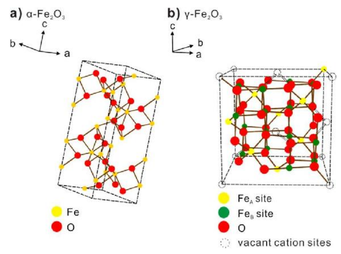


Fig 2. Changes in phages of Iron during Pyrolysis

Objectives

- To modify biochar with Hematite and Goethite and to determine its persulfate activation capacity for SMX removal.
- To determine effects of pH on Persulfate activation and SMX removal
- To determine the radical scavenger (ethanol) and Humic acid effect on persulfate activation.

Materials and Methods

Biochar modification

Pine needles collected were washed and grinded to powder. Suspensions of natural Hematite and Goethite were prepared by mixing in DI water at ratio 50 g L^{-1}, mixed with pine needle powder and was pyrolyzed in tube furnance under continuous N_2 at 600 °C for 30 min.

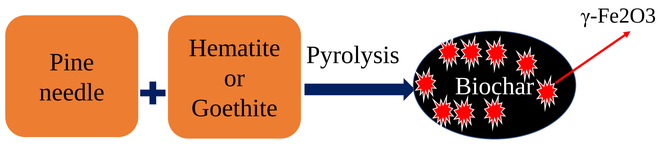


Fig 3. Magnetic modification of biochar

Catalytic degradation

Batch kinetic experiment were conducted in 50 ml plastic tube with SMX solution (10 mg L^{-1}), biochar (1 g L^{-1}) and Persulfate (0.5 mM). Solution pH was adjusted to 4 and 7 by adding HCl or NaOH. 250 mM ethanol and 250 ppm of humic acid was added to test its effect on persulfate activation and SMX removal.

Analysis

SMX concentration was analyzed using HPLC, persulfate using Iodide spectrophotometry method (Liang et al., 2008) and Iron content using ICP-OES after digestion. Carbon and Nitrogen % in biochar were determined using Element analyzer.

Results and discussions

Effect of biochar modification in sorption and persulfate activation

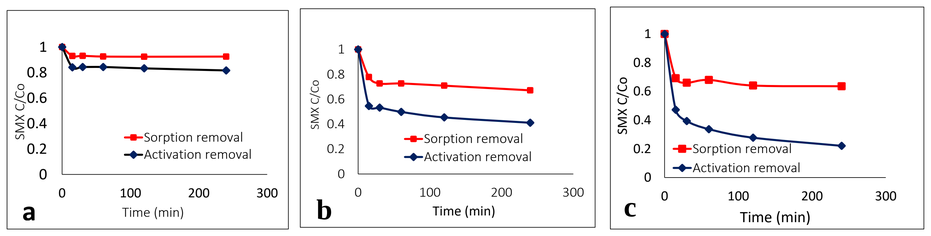


Fig 3. SMX removal kinetics in 4 hour, a = unmodified, b = hematite modified, c = Goethite modified biochar, SMX = 10 ppm, pH = 7, Biochar = 1 g L^{-1} and with PS =0.5 mM in activation removal

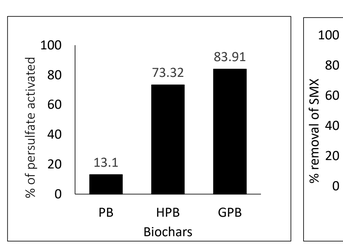


Fig 4. persulfate activation

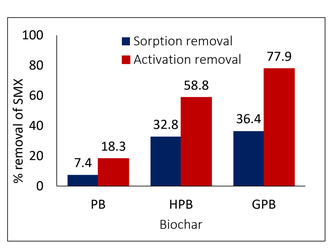


Fig 5. Comparison of sorption and activation removal in 4 hour

- Modification by of pine needle biochar by Hematite and Goethite increased sorption removal of SMX from 7.4 % to 32.8 % and 36.4 % as well as activation removal from 18.3 % to 58.8 % and 77.9 respectively (Fig 5)

- Magnetic property is found in both modified biochar indicates the form of iron present in modified biochar is γ-Fe_2O_3 which has played major role in persulfate activation through transfer of electron to sulfate ion.
- Iron is in the form of α-FeO(OH) or α- Fe_2O_3 in natural hematite (Zhang et al., 2012) without having magnetic property.
- Higher activation capacity of Goethite for persulfate is due to the transformation of Goethite to hematite at 600 °C with large surface area (Liu et al., 2013)

Fig 6. Magnetic property in Biochar

Table1. Element composition in different biochar (weight percentage)

Biochar	% C	% N	% S	Fe (%)
Pine needle unmodified	76.79	0.86	0.16	negligible
Hematite modified	46.34	0.45	0.22	5
Goethite modified	46.05	0.46	0.26	5

- Element analysis shows that 30 % of carbon in biochar is replaced during pyrolysis. ICP analysis showed 5 (w %) iron present in modified biochar. These indicates that biochar is successfully modified having magnetic property which can be recovered from solution using strong magnet.

pH effect on sorption and activation removal

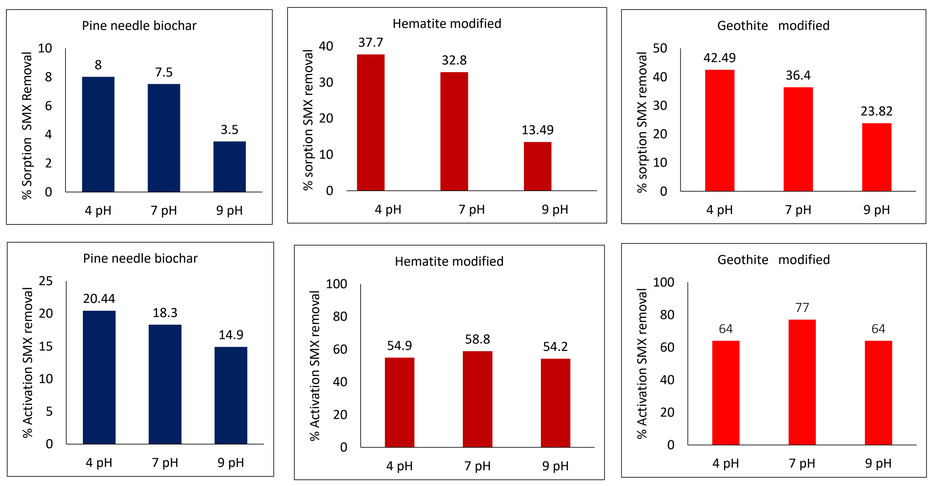


Figure 6. Effect of pH on sorption and activation removal by different biochar

Results and discussions

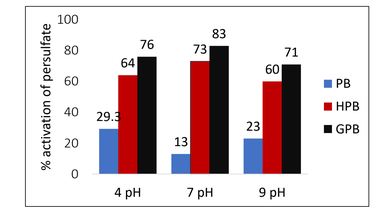


Fig 7. Persulfate activation in different pH

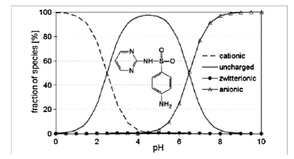


Fig 8 speciation of SMX

Source: Silvia Díaz-Cruz

- Sorption removal is decreased by 7.5 %, 20% and 12% in pH 9 in PB, HPB, GPB respectively.

Effect of Ethanol

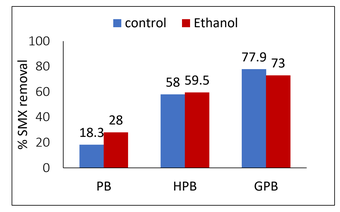


Fig 8. SMX removal in ethanol,

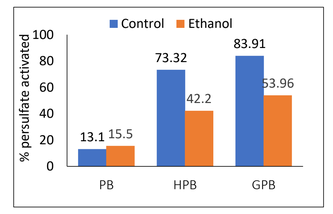


Fig 9. Persulfate activation in 250 mM Ethanol

Negligible effect on activation removal of SMX by ethanol indicates the activation mechanism dominantly governed by the non radical pathway. However, more research need to be done to explain it explicitly.

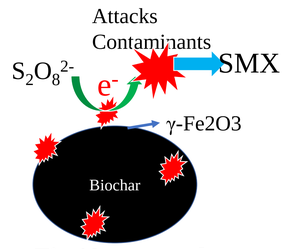


Fig 10 proposed non radical mechanism of persulfate activation for SMX removal

Effect of Humic acid

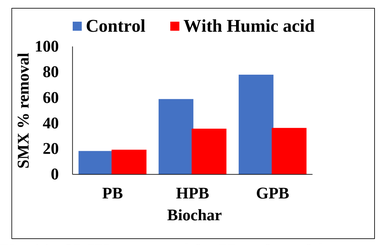


Fig 11. SMX removal in Humic acid,

- humic acid decreased SMX removal by 23 % and 41% in hematite and Goethite biochar respectively (Fig 11).

Conclusions

- Magnetic property in biochar indicates successful biochar modification with γ-Fe_2O_3 and is found efficient in persulfate activation and removal of SMX.
- Solution pH doesn't have much influence in persulfate activation and can work in wide range of for activation.
- Negligible effect of ethanol on activation removal indicates persulfate activation follows nonradical pathway.
- Humic acid decreased SMX removal by 23 % and 41% in hematite and Goethite biochar respectively.

Acknowledgement

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References

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