A Review of Biochar as a Low-cost Adsorbent for Acid Mine Drainage Treatment

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ABSTRACT

Mining industry will give an impact for environment such as acid mine drainage. Acid mine drainage (AMD) is a wastewater that have low pH and high heavy metals content, several companies only use limestone to reducing pH in acid mine drainage, it caused by high environmental management cost, but the problem in acid mine drainage is not only pH. Biochar is a low-cost adsorbent for acid mine drainage treatment. Several studies inform biochar could reduce heavy metals from acid mine drainage. This review will explain about biochar as an adsorbent for heavy metals such as Fe, Mn, Al, Mg, Cu, Zn, Ca, K, Ba, Li, Pb, Ni and Si by recent studies. Depending on biochar types, heavy metals can be removed by different mechanism, thus, biochar is a potential material to solve environmental problems especially caused by mining industry and could reduce environmental management cost.

Keywords : *Biochar, Adsorbent, Acid Mine*

INTRODUCTION

Biochar is pyrogenic carbon from thermal degradation of carbon-rich plant and animal-residues in an oxygen-limited (Safaei *et al.* 2016). Recent studies inform that biochar has attracted much attention due to its promising role in many environmental management issues (Kumar *et al.* 2011) including bio-energy production (Lehmann, 2007) carbon sequestration, soil (Lehmann *et al.* 2006) and environmental management (La, 2019). Recent publications inform that biochar as an adsorbent for wastewater (Li *et al.* 2018; Zhang *et al.* 2019; Mohan *et al.* 2011; Caporale *et al.* 2014) especially AMD that high heavy metals and low pH (Wibowo dan Syarifuddin, 2018). Biochar is increasingly being considerate as an alternative bio-material in water treatment technology (Naswir dan Naswir, 2014).

This paper will describe a comprehensive of recent research finding the theory and developments on the role of biochar to acid mine drainage remediation. The specific object of this paper are follows: (Safaei *et al.* 2016) recent data of biochar production by plants, (Kumar *et al.* 2011) assemble data on the AMD by different types of biochar, and (Lehmann, 2007) discuses the effect of biochar in acid mine drainage (Lehmann *et al.* 2006) review the mechanisms and mathematical models that can be used to describe heavy metal removal by biochar.

Biochar Production

Biochar has been production by every organic materials using pyrolysis. Several study that inform source of biochar such as cassava (Deng *et al.* 2018), coconut (Schneider *et al.* 2018) cattle dung (Sukartono *et al.* 2011) and all of organic matters. Biochar has produced by pyrolysis with limited oxygen and high temperature could make adsorption heavy metals **(Fig. 1)** (Wang *et al.* 2015).

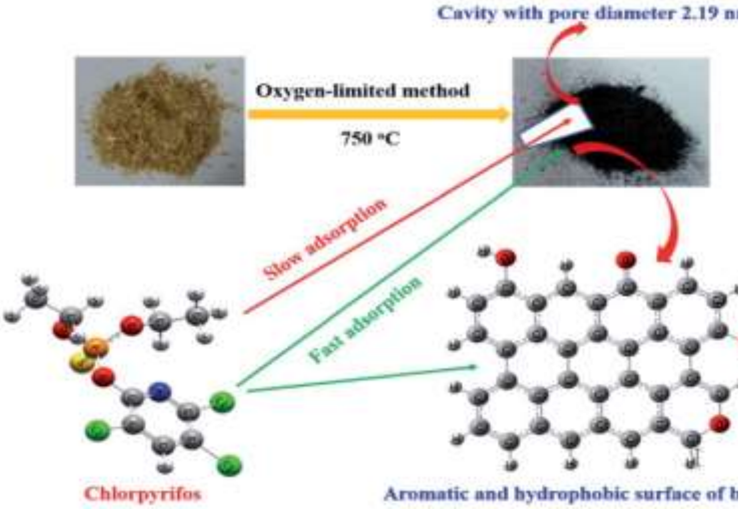

Figure 1. Biochar Production and Adsorption Mechanism

Acid Mine Drainage Treatment Using Biochar

AMD is wastewater has produced by mining industry, AMD have high heavy metals content and low pH. Recent research inform that biochar is good adsorbent for reduce heavy metals in wastewater (Oh and Yoon, 2013). Recent publication about AMD traetment using biochar can see in Table 1.

Table 1. Recent publication about AMD Treatment Using Biochar

Biochar Types	Pyrolysis Temp. (°C)	Adsorption (%)	Pyrolysis (Hour)	Heavy Metals	Reference
The poultry litter pellets	400	Between 30-98	8	Cu, Zn, Mn	(Novak *et al.* 2012)
Oak Wood and Oak Bark	400 and 450	Between 1.41-96.3	-	Na, Ca, K, Ba, Li, Cr	(Caporale *et al.* 2014)
Straws of canola, Soybean and Peanut	400	-	3h 45m	Cu(II)	(Tong *et al.* 2011)
sludge-derived biochar	550	Between 45-60	1	Pb^{2+}	(Lu *et al.* 2012)
Sludge	-	Between 92-98	-	Fe, Al, Ca, Mg, Mn, Zn, Ni, and Cu	(Wei *et al.* 2005)
Common reeds	450	Between 89-98	-	Ca, Mg, K, Na, Cl	(Mosley *et al.* 2015)
Woodchips	60	Between 1-12	48	Fe, S, Ca and Mg	(Li *et al.* 2013)
AMD Sludge and Coal fly	1000	Between 4-20	1	Fe, Al, Si, and Ca	(Wang *et al.* 2013)
Solid Organic	800	Between 35-84	3	Cu	(Oh and Yoon, 2013)

Heavy Metals Removal Mechanism

Several studies inform heavy metals mechanism by biochar including precipitation, complexation, ion exchange, electrostatic interaction and physical sorption **(Fig. 2)**. Adsorption process in biochar has happened by high surface area and pores. Physical sorption desrcibes the removal of metal ions into sorbent pores without formation f chemical bonds. Animals and plants are sources of biochar increasing temperature of carbonization more than 300°C can both effectively remove U, Cu, trough diffusive surface adsorption process (Chai *et al.* 2012).

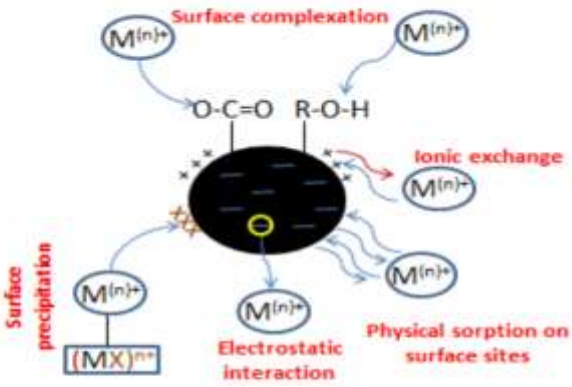

Figure 2. Removal Mechanism of Biochar

Another possible mechanism is sorption of heavy metals through exchange of ionizable cation/proton on biochar surface with dissolved metal species. The efficiency of the ion exchange process in retaining heavy metal contaminants on biochar is closely related to the size of the metal contaminant and surface functional group chemistry of the biochar. Electrostatic interaction between surface charged biochars and metal ions is another mechanism for the immobilization of heavy metals. Prevalence of this mechanism in biochar-metal sorption process is dependent on the solution pH and point of zero charge of biochar (Dong *et al.* 2011). Surface area and porosity are the major physical properties that influence metal sorption capacity of biochar. When biomass is pyrolyzed, micropores form in biochar due to water loss in dehydration process (Bagreev *et al.,* 2001). Biochar pore size is highly variable and encompasses nano (<0.9 nm), micro (<2 nm), and macro-pores (>50 nm). Pore size is important for metal sorption, for instance, biochar with small pore size cannot trap large sorbate, regardless of their charges or polarity (Chen *et al.* 2017) some pores and surface of many biochar source and it's correlation with pyrolysis temperature could see on **Fig 3**

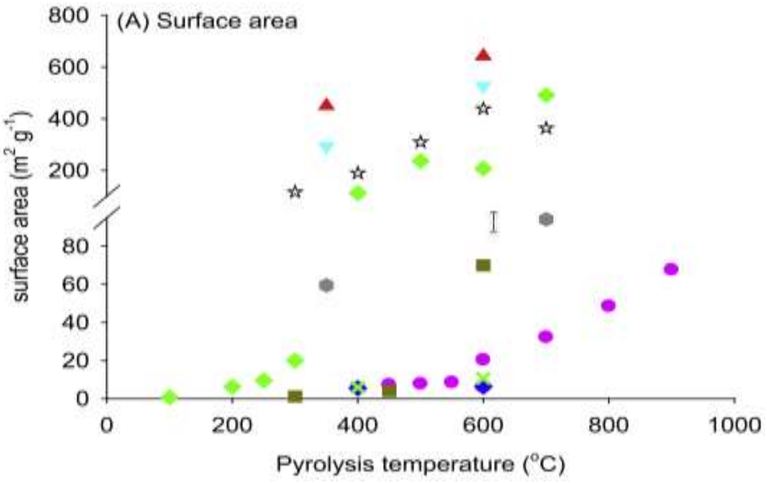

Figure 3. Temperature impact on surface area

Complexion involves information about multi-atom structure with specific metal-ligand interaction. Transition metals with partially filled d-orbitals, having a high affinity for ligands are important binding mechanism for metals (Crabtree, 2005)**.** In particular, oxygen functional groups (carboxyl, phenolic, and lactonic) in low temperature biochars have been demonstrated to effectively bind with heavy metals (Liu and Zhang, 2009) Oxygen content of biochars have also been shown to increase over time, likely due to oxidation of biochar surface and the formation of carboxyl group, thus, metal complexation may increase over time. Some biochar has been utilization to AMD remediation with different removal heavy metals mechanism such as cotton seed hull char to remove Cd, Cu, Ni and Pb with complexation of metals by oxygen functional group (Uchimiya, 2011), risk hush carbon to remove Hg and Zn with ion exchange between H^+, Zn^{2+} and Hg^{2+} removal mechanism (El-Shafey *et al.* 2010), flax shive carbon to remove Cd with ion exchange between H^+ and Cd^{2+} removal mechanism (El-Shafey *et al.* 2002), beech wood char for removal Cu with complexion of Cu by carboxyl functional groups mechanism (Borchard *et al.* 2012), digested animal char for removal Pb, Cu, Ni and Cd with precipitation removal mechanism (Inyang *et al.* 2012) and bone char to removal Cd, Cu and Zn with surface adsorption and diffusion into pores mechanism (Choy and McKay, 2005).

Mathematical Modeling

Mathematical models of biochar sorption could describes by thermodynamic adsorption, kinetics adsorption include pseudo-first orde model, pseudo-second model, elovich model, and diffusion model, and than adsorption isoterm include langmuir model, freundlich model, langmuir-freundlich and langmuir-langmuir model and filtration model. Thermodynamic models are tools to describe metals sorption process and explore it's mechanisms. Metals sorption of thermodynamic model of biochar can described as either exothermic and endothermic. Exothermic sorption is sorption decreases with increasing temperature and endothermic is sorption increases with increasing temperature. Thermodynamic parameters are often used to characterize thermodynamic such as enthalpy ΔH0, entropy, ΔS0, and Gibb's free energy, ΔG0, these parameters could computed by these equations bellow (Chen *et al.* 2011):

$$Ke = \frac{qe}{Ce}$$

$$\Delta G = -RTlnKe$$

$$\Delta G = \Delta H - T\Delta S$$

qe (mg/g) is the amount of heavy metals adsorbed on biochar at equilibrium, Ce (mg/L) is the equilibrium concentration of heavy metals in the solution; R (J/mol_K) is the gas constant (8.314), T (K) is the absolute temperature, and Ke (L/g) is the adsorption equilibrium constant. By plotting ln Ke against 1/T, the values of ΔHo and ΔSo can be determined from the slopes and intercepts, respectively. The values of ΔGo can then be calculated from the corresponding values of ΔHo and ΔSo. Positive ΔHo values indicate that the sorption reaction is endothermic, supported by an increase in qe (mg/g) with increasing temperature. On the other hand, negative ΔGo values suggest a spontaneous sorption process with increasing metal sorption at higher temperatures. Positive values of ΔSo may reflect an affinity of the carbon sorbent for the metal ions (Lu *et al.* 2009). Free energy, ΔGo (KJ/mol) could also provide information to distinguish physical sorption (ΔGo, -20 to 0 KJ/mol) from chemisorption (ΔGo,-400 to -80 KJ/mol) processes (Liu and Zhang, 2009). Several studies has described kinetic adsorption models such as first/pseudo first order, second/pseudo second order, Elovich, and intraparticle-diffusion model. These model are describing below:

$qt = qe\ (1 - e^{-kt})$ (Pesudo first order)

$qt = \frac{K2qe^2t}{1+K2qet}$ (Pseudo second order)

$qt = \frac{1}{\beta}ln(\alpha\beta t + 1)$(Elovich)

$qt = K1t\ 1/2 + w$(Intraparticle diffsuion)

Where qt (mmol kg-1) and qe (mmol kg-1) are the amounts of metal sorbed at time t and at equilibrium respectively; k1 (h-1) and k2 (kg mmol-1 h-1) are the first-order and second order apparent sorption rate constants, respectively; α (mmol kg-1 h-1) and β (kg mmol-1) are the initial Elovich sorption and desorption rate constant at time t, respectively, K1 is the intra-particle diffusion rate constant (mmol kg-1h-0.5), and W (mmol/kg) is a constant.

Adsorption isoterm and qeilibrium model are used to explore how an adsorbate interacts with an adsorbent (Chiou and Li, 2002), equilibrium models to describe isoterm of metals on biochar include Freundlich, Langmuir, Freundlich-Langmuir and double Langmuir model, these models are following:

$S = \frac{SmaxKc}{1+KC}$(Langmuir)

$S = K_f\, C^n$ (Freundlich)

$S = \frac{SmaxKc}{1+KC}$(Langmuir-Freundlich)

$S = \frac{Smax1K1C}{1+K1C} + S = \frac{Smax2K2C}{1+K2C}$(Double Langmuir)

where S (mmol/kg) is the amount of metal adsorbed and Smax (mmol/kg) is the maximum amount of metal adsorbed in mmol/kg; S_{max1} (mmol/kg) and S_{max2} (mmol/kg) are the maximum amounts of metal adsorbed related to the sorption and precipitation processes, respectively; K (L/mmol) is the Langmuir adsorption constant related to the interaction bonding energy and Kf (mmol(1- n)Ln/kg) is the Freundlich equilibrium constant in L/mmol; K_1 and K_2 are the Langmuir bonding terms related to sorption and precipitation energies in L/mmol, respectively; C is the equilibrium solution concentration in mmol/L of the sorbate; and n is the Freundlich linearity constant

CONCLUSION AND FUTURE DIRECTION

This paper has presented affect of heavy metals content in acid mine drainage removal by biochar, predominant heavy metal removal mechanisms vary for different biochars and metal contaminants. For instance, transition metals are commonly adsorbed by precipitation and complexation mechanisms onalkaline biochars (plant or animal) produced by high temperature. Various biochar and its sources have been discussed in depth included temperature, heavy metals, percent sorption, pyrolysis duration and mechanism of removal heavy metals. Recent studies has made biochar by pyrolysis in high temperature with furnace. Experimental and modeling studies for create biochar in simple technology to reduce heavy metals in packed columns are highly recommended for future studies.

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