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Biochar-Materials for Remediation on Swamplands: Mechanisms and Effectiveness

Biochar-Bahan Remediasi Tanah Rawa: Mekanisme dan Efektivitasnya

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Abstract. The purpose of this paper is to synthesize all research results qualitatively to explore the potential of biochar as a remediation agent in swamps, including its mechanism, and effectiveness. The soil in swampland is characterized by the presence of pyrite (FeS_2) which results in high acidity (soil pH <3.5). The reduction process in swamps produces high amounts of ferrous iron (Fe^{2+}) which is then released into the environment. The mechanism of iron (Fe) poisoning is indicated by the inhibition of nutrient uptake because the roots are covered with iron. This disturbs the root function as a nutrient absorber. Recent research shows that biochar could be used as an approach to reduce soil pollution in swamps through metal immobilization processes. This review paper uses a qualitative method with meta-aggregation approach based on the Francis-Baldesari method (2006). Principally, the soil remediation mechanism using biochar does not remove metals but accumulate them into hydroxide or carbonate deposits with the help of existing microorganisms. Provision of rice husk Biochar can increase the pH value reaching ≥ 5.0 and grain yield by 20% in intensively cultivated tidal swamps. Increasing the pH value of the soil will support the formation of Fe hydroxide deposits which are accumulated on rice roots.

Keywords: Ferro iron, / Soil acidity / Tidal swampland / Soil contamination / Immobilization of metal

Abstrak. Tujuan penulisan paper ini adalah mensintesis seluruh hasil penelitian secara kualitatif untuk menggali potensi biochar sebagai bahan remediasi pada lahan rawa meliputi mekanisme, dan efektivitasnya. Tanah di lahan ini dicirikan oleh keberadaan pirit (FeS_2) yang menghasilkan keasaman tinggi (pH tanah <3,5). Proses reduksi di lahan rawa menghasilkan besi ferro (Fe^{2+}) dalam jumlah tinggi dan dilepaskan ke lingkungan. Mekanisme keracunan besi (Fe) ditunjukkan dengan terhambatnya serapan hara karena perakaran diselimuti oleh besi sehingga fungsi akar sebagai penyerap unsur hara terganggu. Penelitian terbaru menunjukkan bahwa pemanfaatan biochar sebagai salah satu pendekatan untuk mengurangi pencemaran tanah di lahan rawa melalui proses immobilisasi logam. Paper review ini menggunakan metode kualitatif berdasarkan metode Francis-Baldesari (2006) dengan pendekatan metaagregasi (meta-aggregation). Mekanisme remediasi tanah menggunakan biochar prinsipnya tidak menghilangkan logam tetapi mengakumulasinya menjadi endapan hidroksida maupun karbonat dengan bantuan mikroorganisme yang ada. Pemberian Biochar sekam padi dapat meningkatkan nilai pH mencapai $\geq 5,0$ dan hasil gabah sebesar 20% di lahan rawa pasang surut yang intensif dibudidayakan. Peningkatan nilai pH tanah mendukung pembentukan endapan hidroksida Fe yang diendapkan pada akar padi.

Kata kunci: Besi ferro / Keasaman tanah / Pencemaran tanah / Immobilisasi ion logam

INTRODUCTION

The development of agricultural activities in swamps can bring large amount of heavy metals to the local environment due to various physico-chemical processes such as: adsorption, ligand exchange, and sedimentation. Swamps have hydrological and environmental functions that are important for all living things. Therefore, swamps must

be protected and preserved. Swamp land must be used wisely by applying thorough planning, appropriate technology, and proper management. Soil acidification is a problem in swamplands. High soil acidity causes the increasing Fe and Al solubility, which makes agricultural crops difficult to grow normally. In general, the problem of heavy metals in acid sulphate soils is caused by pyrite oxidation process, such as high concentrations of aluminum and iron. Aluminum

toxicity potentially produces complex AI interaction with the apoplast, plasma membrane, and symplast in plant tissue (Singh *et al.* 2017).

Saeni (1997) reported that heavy metal elements are potentially cause pollution in the environment, i.e. Fe, As, Cd, Pb, Hg, Mn, Ni, Cr, Zn, and Cu. These elements have high level of toxicity and extensively used. Meanwhile, the United State Environment Protection Agency (US EPA) lists heavy metals which are the main dangerous pollutants, namely Sb, Ag, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Sr, Ag, and Zn (Sukhendrayatna 2001). On the other hand, there are also heavy metals such as Cr, Cu, Fe, Mn, Mo which are essential micro nutrients for plants, but it will be toxic to plants if the concentration in the soil exceeds the critical limit. Alloway (1995) states that excess heavy metals in the soil would not only poisoning the plants and organisms, but it could also have implications as environmental pollution.

The efforts to remediate soil contaminated with heavy metals by implementing environmental rehabilitation strategies are generally very expensive (Onrizal 2005). Therefore, it is important to develop an inexpensive and environmentally friendly strategy by applying immobilization techniques that use soil amendments such as: biochar, manure, compost, and coal fly ash (Palansooriya *et al.* 2020). Biochar is an organic biomass that can be developed at the farmer level to solve the problems of polluted environment. The utilization of biochar is one of the prospective agricultural wastes management efforts to encourage the optimization of suboptimal and degraded lands (Nurida 2014). In the soil, biochar provides a good habitat for soil microbes, for example bacteria, that help to breakdown the nutrients into the form that can be absorbed by plants (Annisa and Nursyamsi 2016a). Biochar is produced through a pyrolysis process under the conditions of limited oxygen supply and at a temperature of 300-700°C (Lehmann and Joseph 2012). Through adsorption and physicochemical reactions, biochar is potentially reducing bioavailability and leaching heavy metals and organic pollutants in the soil due to its wide surface area and the high capacity to absorb heavy metals (Park 2011).

The purpose of this paper is to synthesize all research results qualitatively to explore the potential of biochar as a remediation agent in swamplands, including its mechanism and effectiveness.

REVIEW METHODOLOGY USED

This paper uses a systematic review method that summarizes the results of primary research related to the use of biochar on absorbing heavy metals. It also to present a more comprehensive and balanced fact using a qualitative approach.

The steps used in the preparation of this paper follows a qualitative review systematic (Francis-Baldesari 2006), namely: (1) formulating the review question, (2) conducting a systematic literature search, (3) screening and selecting appropriate research articles, (4) conducting qualitative analysis and synthesis, and (5) compiling papers.

FINDINGS

Biochar Characteristics as Remediation Material

Biochar is produced by applying thermochemical techniques (pyrolysis) using biomass from various sources, therefore the function of biochar as a soil ameliorant is vary. Biochar has pores with high carbon content originating from the pyrolysis process at temperature of 300-700°C under limited oxygen conditions (Komaryati *et al.* 2012). When this biomass waste is burned, it will produce aromatic organic material having carbon content 70-80% (Lehmann *et al.* 2006). Thi *et al.* (2015) reported that the element of carbon can help to increase soil pH due to its ash content. Hence, it can act as a liming agent. There are several types of biochar, namely: woody debris, crop residues, food processing waste, and manure. Each of them is significantly different in organic content and ash composition which influence the quality of the produced biochar.

According to Guo *et al.* (2020), the carbonization technique (pyrolysis) used in the process of making biochar also affects the quality and characteristics of the produced biochar. There are three methods that can be used to manipulate the carbonization process, namely: (1) setting the pyrolysis temperature, (2) setting the dwell time, and (3) setting the heating rate. The higher pyrolysis temperature will accelerate the carbonization process which allows biomass transformation to complete pyrolysis stage in a shorter time (Song and Guo 2012; Chen *et al.* 2017). Meanwhile, the dwell time to achieve complete pyrolysis is determined by the pyrolysis temperature and heating rate, starting from seconds to days. According to Chun *et al.* (2004), the

biochar produced from an incomplete pyrolysis will contain a portion of C (carbon) that has not been carbonized. It could be indicated by the crystal character of the precursor material (intermediate product). The chemical composition of cellulose or holocellulose - total polysaccharide fraction, lignin, ash and extractives from biomass affect the thermal degradation process.

To obtain activated carbon from biomass, an activation process of charcoal as an intermediate product (precursor) is carried out from pyrolysis carbonization at 350-500°C (Chuenklang *et al.* 2002). Activated carbon is a good adsorbent because of it has better adsorption power and larger surface area than other adsorbents (Walas 1990). According to Sudibandriyo *et al.* (2003), a good activated carbon has a large surface area and high adsorption capacity. Characteristics of surface area, pore volume, and aliphatic functional groups affect the affinity of biochar (Gray *et al.* 2014) which depends on pyrolysis conditions and the type of biomass (Das and Sarmah 2015). The characteristics and quality of biochar that is based on the type of biomass and its carbonization process are shown in Table 1.

Metal Elements in Swampland: Stability and Toxicity

Metal Stability in Swamplands

Soils in swamplands are generally formed from marine sediment and rich of organic matter in sea / brackish water environment which contains dissolved sulfate (SO_4) compounds (Annisa and Hanudin 2013). It usually has high pyrite content. Problems in swamps arise when pyrite is oxidized due to the presence of O_2 , thus changing the solubility of Fe^{3+} and SO_4^{2-} and causing the increase of the solubility of some elements such as: Al, Fe, and Mn. The final result of pyrite oxidation is the formation of H^+ ions which will result in the decrease of soil pH and then some of these ions are also used to oxidize Fe^{2+} to Fe^{3+} (Breemen and Buurman 2002). Annisa and Purwanto (2012) say that the decrease of pH below 4 will cause ferric iron (Fe^{3+}) in the soil to be dissolved and oxidizes pyrite rapidly. The stable form of iron is in the form of ferrous iron (Fe^{2+}).

In moderate acidity conditions, FeOOH will be dissolved into Fe^{2+} , while ferric iron (Fe^{3+}) will be dominant in very oxidative conditions with redox potential values >400 mV and pH <2 (Annisa and Hanudin 2013). Ponnampurna (1977) reported that

Table 1. Characteristics and quality of biochar based on the type of biomass used and the carbonization process

Tabel 1. Karakteristik dan kualitas biochar berdasarkan jenis biomassa yang digunakan dan proses karbonisasinya

Sources of Biomass	Pyrolysis Temperature	Biochar characteristics based on biomass sources								References
		Biochar Physical Properties	Biochar Chemical Properties							
		Specific Surface Area	pH	Ash content	C-org	N-tot	P- tot	K-tot	CEC	
	°C	m ² g ⁻¹%g kg ⁻¹	cmol _c kg ⁻¹	
Rice husks	400	-	8.6	27.5	54.1	4.9	-	-	-	Nwajiaku <i>et al.</i> (2018)
Rice husks	500	-	9.2	-	47.8	-	-	-	17.6	Ghorbani <i>et al.</i> (2019)
Rice husks	600	114.9	9.9	47.0	54.5	11.0	-	-	-	Windeatt <i>et al.</i> (2014)
Rice husks	700	-	10.7	35.6	54.5	3.6	-	-	-	Nwajiaku <i>et al.</i> (2018)
Corncob	550	56.4	-	-	81.4	12.2	-	-	-	Wijitkosum <i>et al.</i> (2019)
Corncob	500	-	9.3	6.3	70.3	6.5	-	-	24.0	Setiawati and Annisa. (2020)
Corn stalks	300	-	7.2	8.2	53.2	26.1	-	29.0	-	Liu <i>et al.</i> (2018)
Corn stalks	400	-	8.6	14.0	58.1	26.9	-	43.5	-	Liu <i>et al.</i> (2018)
Corn stalks	500	-	10.0	16.3	59.7	24.3	-	50.0	-	Liu <i>et al.</i> (2018)
Corn stalks	600	-	9.8	17.3	61.8	17.3	-	50.5	-	Liu <i>et al.</i> (2018)
Palm oil fruit shells	600	220.0		6.7	90.6	9.0	-	-	-	Windeatt <i>et al.</i> (2014)
Coconut shells	600	222.5		4.1	93.9	4.0	-	-	-	Windeatt <i>et al.</i> (2014)
Hardwood	400	15.4	7.5	3.2	79.0	2.5	0.18	3.0	7.9	Tian <i>et al.</i> (2016)
Hardwood	500	26.6	8.2	4.2	84.8	3.0	0.34	3.6	7.5	Tian <i>et al.</i> (2016)
Durian wood	500	-	8.9	5.2	71.9	3.6	-	-	25	Setiawati and Annisa (2020)
Softwood	400	-	7.3	-	74.6	2.5	-	2.5	-	Gezahegn <i>et al.</i> (2019)
Softwood	600	-	8.1	-	88.6	3.8	-	1.8	-	Gezahegn <i>et al.</i> (2019)

under stagnant conditions the range of Fe^{2+} levels in swamps was 0.07 to 6,600 $\text{mg kg}^{-1} \text{Fe}^{2+}$, depending on pH, organic matter, levels and reactivity of Fe^{3+} . This is in line with Annisa and Nursyamsi's (2016) research that the concentration of ferrous iron (Fe^{2+}) in soils in swamps during rice growth ranges from 782-1,308 mg kg^{-1} . The reduction process of SO_4^{2-} and Fe (III) oxides in swamps occurs in a flooded (anaerobic) condition. It could increase soil pH due to proton consumption in the process (Muhrizal *et al.* 2006).

The process of reducing Fe (III) and SO_4^{2-} is carried out by iron and sulfate reducing bacteria which is described by the following equation (Dent and Pons 1995):

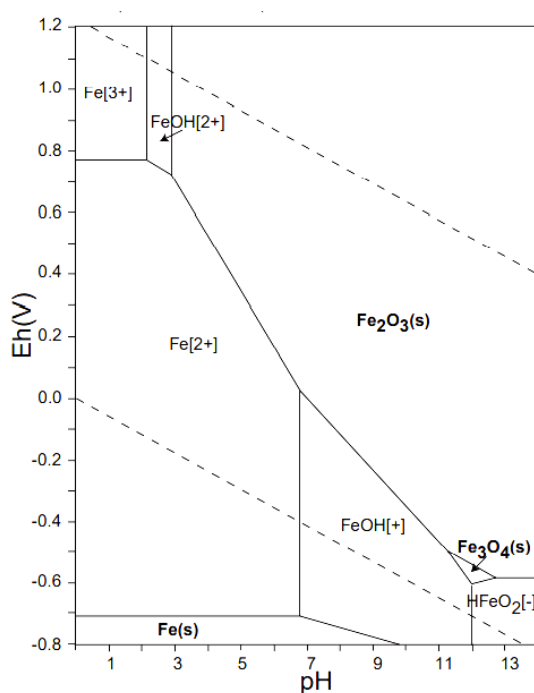
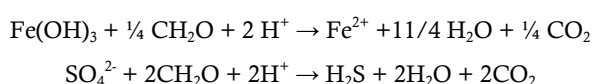


Figure 1. Stability diagram of the form of Fe at several Eh and pH values (Source: Huang 2015)

Gambar 1. Diagram stabilitas bentuk Fe pada beberapa nilai Eh dan pH (Sumber: Huang 2015)

Satawathananont *et al.* (1991) reported that changes in soil pH and Eh affect the stability and solubility of metallic minerals in soil solutions. The research by Annisa and Nursyamsi (2016a) shows that there is negative correlation between soil redox conditions (Eh) and ferrous iron concentration (Fe^{2+}) with a value of $r = -0.856$ in rice cultivation in swamplands, where the lower the redox potential value,

the higher the concentration of ferrous iron (Fe^{2+}) in the soil. This is related to the intensification of the reduction process in the soil. Fe stability due to the effect of Eh and pH is shown in Figure 1.

Metal Toxicity in Swamplands

Metal elements such as: Fe, Al, and Mn in swamplands are micro nutrients needed by plants. However, excessive availability of these elements would become toxic to plants. The tolerated limit of iron poisoning in rice plants reaches ≤ 300 ppm depending on the rice variety. This is in line with Verloo's (1993) statement that high levels of metal in the soil do not necessarily result in phytotoxicity in plants because the rate of metal uptake by plants is not correlated with the rate of increase in metal content in the soil. This statement is supported by the transfer coefficient calculation method using formula:

$$T = \frac{\text{The amount of increased levels in the plant}}{\text{The amount of increased levels in the soil}}$$

Where, the T value varies widely between heavy metal elements and between parts of plants and is influenced by CEC and soil pH. If the T value > 1 , the heavy metal content in the soil will be potentially toxic to plants. The bioavailability of metals in soil is strongly influenced by (Verloo 1993): (1) equilibrium reactions, (2) soil cation exchange capacity (CEC), (3) complexing reactions, (4) pH of the solution which directly affects the dissolution of the heavy metal elements, (5) Anions in soil solution, and (6) Soil redox potential.

Among the soil types in the world, soil types in swamps cause Fe toxicity in rice (Becker and Asch 2005). India, Southeast Asia, West and Central Africa and Brazil reported that Fe toxicity in plants was a major factor affecting grain yield and rice growth (NRCS 2005; Mahender *et al.* 2019; Gridley *et al.* 2006). Excess iron in rice causes damage and disruption of cellular homeostasis tissue. The effect of Fe toxicity on rice is shown in Figure 2.

In plants, the solubility of Fe varies depending on pH. According to Li *et al.* (2015) iron toxicity will inhibit primary root extension and lateral root growth. If Fe uptake by roots is high and translocated to leaves via transpiration flow, it will cause Fe accumulation in plant tissue (Briat and Lobréaux 1997). The form of Fe^{2+} ions in the plant tissue will be oxidized to Fe^{3+} ions, where some of the ions settle and decrease their mobility and reactivity. The other Fe^{3+} ions are reactive

and mobile in cytosol, which if there is no chelating process will cause toxicity to rice plants. Excess Fe ion conditions in plant cells will damage biological processes and cause leaf bronzing symptoms due to cell death (Aung and Masuda 2020).

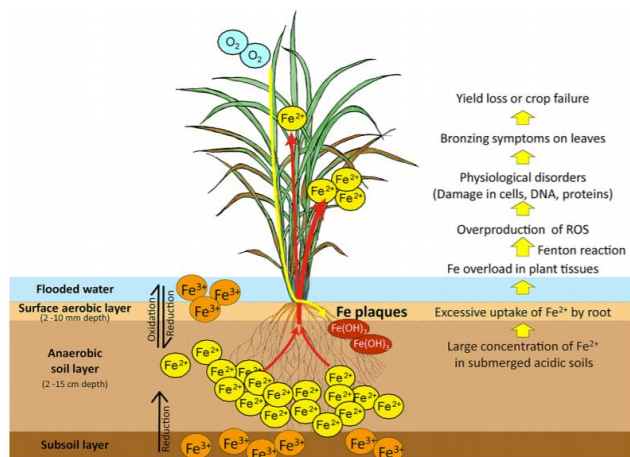


Figure 2. Scheme of iron toxicity and reduction process in inundated soils with low pH conditions (Source: Aung and Masuda 2020)

Gambar 2. Skema proses reduksi dan toksisitas besi di tanah tergenang dengan kondisi pH rendah (Sumber: Aung and Masuda 2020)

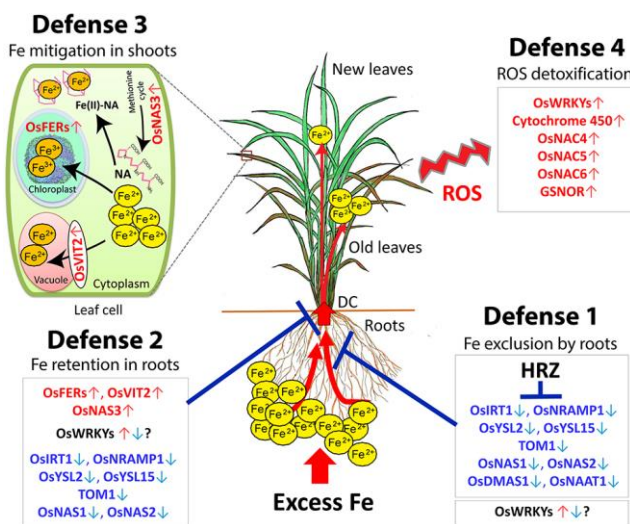


Figure 3. A hypothetical model of four defense mechanisms for rice plants against an excess of Fe in soil solution (Source: Aung and Masuda 2020)

Gambar 3. Model hipotetik empat mekanisme pertahanan tanaman padi terhadap kelebihan Fe di larutan tanah (Sumber: Aung and Masuda 2020)

Plants use a variety of methods to desorb metals from the soil matrix (Sheoran *et al.* 2009). Rice plants

have four defense mechanisms against iron toxicity. The model of the tolerance mechanism for rice plants to an excess of Fe in the soil solution is shown in Figure 3.

In conditions of Fe excess, rice plants use 4 defense mechanisms, namely:

- 1. Root-based Fe exclusion mechanism.** This mechanism inhibits Fe uptake by roots by oxidizing Fe^{2+} ions to Fe^{3+} in the rhizosphere and depositing it on the root surface. It is then forming Fe plaque which functions to block Fe^{2+} uptake by root tissue (Becker and Asch 2005). Genotypes that are tolerant of Fe excluder using mechanism 1 are indicated by the high formation of Fe plaque on the surface of plant roots (Mahender *et al.* 2019). This mechanism protects plants in low Fe conditions
- 2. Fe retention mechanism in root tissue.** When the concentration of Fe in the soil solution increased, the defense mechanism 1 would not be able to prevent the uptake of Fe by the roots. Therefore, the second defense mechanism would work by blocking the translocation of Fe from root to leaf and accumulating it in the root tissue. This mechanism precipitates >90% Fe in the root apoplast during excessive Fe concentration in soil solution (Tadano 1975). Hence, the excessive Fe accumulation in leaves does not occur (Becker and Asch 2005).
- 3. Mechanism of Fe storage in shoots.** Rice plants can hold limited amount of Fe in the root tissue. When mechanisms 1 and 2 are unable to hold the excess of Fe in the roots, then mechanism 3 works by translocating Fe into leaves and storing it in shoots and starting to use the chelation process. Nugraha's research (2016) shows that several genotypes of swamp rice, such as Siam Saba, Mahsuri, Margasari, and Pokkali, perform a third mechanism to avoid iron toxicity as evidenced by high concentrations of Fe in shoots with less bronzing symptoms on leaves, and high grain yields.
- 4. Mechanism of Fe Storage in Vacuoles.** In severe poisoning conditions, most of the Fe will be accumulated in the cytosol by plants.

Remediation Using Biochar in Swamplands: Mechanism and Effectiveness

Metal Adsorption Mechanism with Biochar

In situ metal stabilization can be done by adding commonly used soil amendments such as lime and organic matter in an effort to reduce metal bioavailability and minimize its absorption by plants

(Komárek *et al.* 2013). The order of stability of divalent cations (metal cations) in the metal-organic binding process in soil solution is: $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$. Biochar is an adsorbent that can be used to decontaminate agricultural soil. The hydrophobic properties with high specific surface area ($800\text{--}1200 \text{ m}^2 \text{ g}^{-1}$) and porous make biochar as the best adsorbent to remediate metal contaminants in soil (Das and Sarmah 2015). Carbonization removes C = O groups which are identical to carboxylate groups because the absence of oxygen on the heating process will decompose the oxygen functional groups from the carbon surface. Shafeeyan *et al.* (2010) reported that carboxylic groups (C = O) will begin to be decomposed on heating at a temperature of 400°C . Increasing the temperature to 600°C will completely decompose the C = O group. Decomposition of Carbon Functional Groups under Inert Conditions is shown in Figure 4.

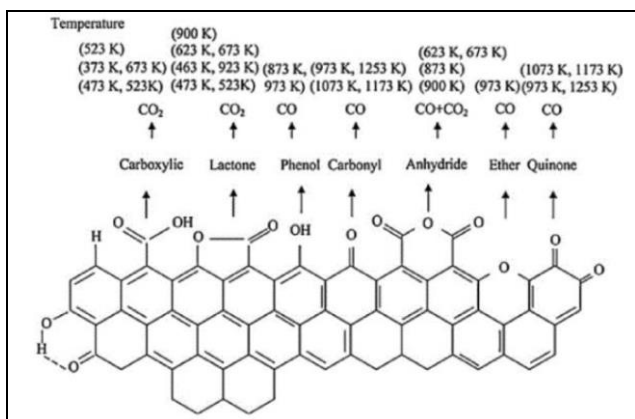


Figure 4. Carbon functional group decomposition in inert conditions (Source: Pratama *et al.* 2018)

Gambar 4. Dekomposisi gugus fungsi karbon dalam kondisi inert (Sumber: Pratama *et al.* 2018)

The carbonization process caused changing in the O-H group, from hydrogen bonds to monomer groups. This is due to the aromatization of cellulose compounds into poliaromatic structures during the carbonization process, consequently the O-H groups will stick to the aromatic compounds. The research of Pratama *et al.* (2018) showed that the higher the carbonization temperature, the wider the surface area of the biochar produced. According to Jeong *et al.* (2015), an increase in the surface area of carbon is due to more evaporation of volatile compounds, therefore they can form empty spaces and pores in the carbon structure. The porous structure with a large surface area of the biochar provides a shelter for beneficial soil

microorganisms such as mycorrhizae and bacteria which affect the binding of cations and anions.

The adsorption method is one of the most efficient methods to reduce metal content in the soil (Lelifajri 2010). Adsorption of Fe metal uses biochar through several mechanisms, namely: (1) formation of the innersphere and outersphere surface complexes. In the soil solution, metals act as Lewis acids (electron acceptors) which react with functional groups (-OH, -SH, and -COOH) on the surface of the biochar to form a surface complex (innersphere complex) to produce a compound in the form of a Lewis salt (Reaction 1), whereas the Outersphere exchange complex is formed when a water molecule binds to a biochar functional group and an iron ion (Reaction 2); (2) Electrostatic bonding, (3) ion exchange-based adsorption and (4) Fe precipitation with organic ligands to form an organo-mineral (Fe-OH) complex on the surface and precipitate (reaction 3). Lu *et al.* (2012) reported that innersphere and outersphere adsorption and surface precipitation have contribution on stabilizing Fe metal in soil solution. The mechanism by which biochar stabilizes metals in soil solutions is shown in Figure 5.

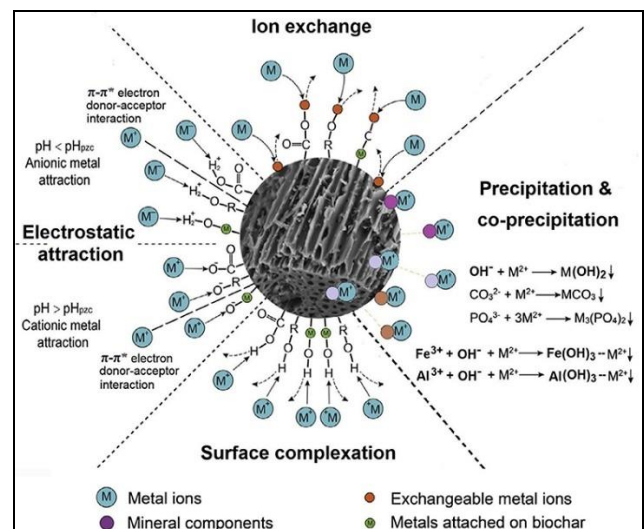
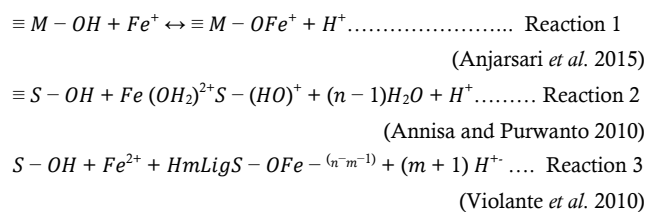


Figure 5. Biochar mechanism to stabilize metals in soil solution (Source: Tan *et al.* 2015)

Gambar 5. Mekanisme biochar untuk menstabilkan logam di larutan tanah (Sumber: Tan *et al.* 2015)

Carboxyl, hydroxyl, and especially phenolic groups on the surface of the biochar are effective in binding metal contaminants in soil solutions (Uchimiya *et al.* 2011). Identification of the possible existence of functional groups of compounds contained in biochar that play a role in the iron adsorption process in soil solutions can be identified through functional group analysis with Fourier-transform infrared spectroscopy (FTIR).

The Effectiveness of Biochar as a Remediation Agent in Swamplands

Biochar has the ability to reduce the activity of metal ions in soil solutions depending on its quality. Biochar that is produced at high temperatures ($\geq 600^\circ\text{C}$) generally has high surface areas. Therefore, it is very good for metal adsorption or physical absorption but does not contain nutrients. On the other hand, biochar which is formed at temperature of $400\text{--}500^\circ\text{C}$ has lower surface area with diverse functional groups and

relatively contains nutrients (Zhen *et al.* 2013). Uchimiya *et al.* (2010) reported that biochar application can increase pH and cation exchange capacity, as well as increase metal immobilization in the soil. Guo *et al.* (2020) reported that in general soil improvement with biochar at doses of $>2.0\%$ by weight helps stabilize metals and accumulates toxic elements in the soil. The efficiency of biochar as a remediation agent to stabilize metals depends on the source of biochar, particle size, changes in dose, chemical properties of pollutants, and the types of soil in swamps. Several research results related to soil remediation with high Fe content using biochar are shown in Table 2.

CONCLUSION

Literature data show that biochar has the capacity and efficiency to stabilize metals and reduce soil contamination depending on the biochar source, dosage, soil type, and metal type. The mechanism of

Table 2. Some results of soil remediation research on soils with high Fe content using biochar

Tabel 2. Beberapa hasil penelitian remediasi tanah pada tanah dengan kadar logam Fe yang tinggi menggunakan biochar

No	Biochar sources	Soil types	Commodities	Biochar effects	Mechanisms	References
1	Rice husk biochar	Tidal land, hydro-topography class B, Central Kalimantan	Rice	<ul style="list-style-type: none"> Reducing Fe levels by 1.97% Increasing soil pH by 0.65 units Increasing grain yield 	<ul style="list-style-type: none"> Formation of iron plaque on the root surface Metal stabilization through adsorption by biochar 	Masulili <i>et al.</i> (2010)
2	Rice Husk Biochar	Tidal land, hydro-topography class B, Central Kalimantan	Rice	<ul style="list-style-type: none"> Increasing soil pH Increasing grain yield 	<ul style="list-style-type: none"> Metal stabilization through adsorption by biochar 	Setiawati and Annisa (2020)
3	Durian wood biochar	Tidal land, hydro-topography class C, South Kalimantan	Maize	<ul style="list-style-type: none"> Increasing soil pH Increasing the weight of corn cobs 	<ul style="list-style-type: none"> Metal stabilization through adsorption by biochar 	Setiawati and Annisa (2020)
4	Biochar of Rice Husk + Agricultural Waste Compost	Tidal land, hydro-topography class B, South Kalimantan	Rice	<ul style="list-style-type: none"> Increasing grain yield by up to 28% Reducing methane (CH_4) emissions 	<ul style="list-style-type: none"> Binding metal by biochar through an adsorption process 	Annisa and Mukhlis (2020)
5	Biochar of Rice Husk + Agricultural Waste Compost	New openings tidal land, hydro-topography class B, South Kalimantan	Rice	<ul style="list-style-type: none"> Increasing soil pH Increasing grain yield by up to $>20\%$ Reducing methane (CH_4) emissions 	<ul style="list-style-type: none"> Binding metal by biochar through an adsorption process 	Annisa and Nursyamsi (2016b)

metal absorption by biochar is carried out by: formation of innersphere and outsphere surface complexes, electrostatic bonds, ion exchange-based adsorption and precipitation of Fe with organic ligands to form an organo mineral complex (Fe-OH). The abundance of surface functional groups and the biochar CEC determines its ability to adsorb metals. Provision of biochar in tidal swamplands can stabilize the toxic element of iron (Fe) by forming iron plaque on the root surface and metal adsorption by biochar, thereby increasing soil pH and grain yields reaching >20%.

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