Biological Forum – An International Journal **15(10): 1317-1321(2023)**

ISSN No. (Print): 0975-1130
ISSN No. (Online): 2249-3239

Mechanism of Redox Reaction in Soil Chemistry

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(Received: 21 August 2023; Revised: 25 September 2023; Accepted: 07 October 2023; Published: 15 October 2023)
(Published by Research Trend)

ABSTRACT: Soil chemical reactions involve both oxidation and reduction reactions, which together are called redox reactions. Soil pH mainly controls the redox reaction process. Another indicator of a redox reaction is redox potential. The relationship between soil pH and Eh is based on soil condition; acid soil raises pH due to a decrease in redox potential, whereas alkaline soils are antithetical. The changes in these reactions in soil interrupt the presence of microorganisms and their growth development. Some microorganisms require oxidized elements for their survival, and the enzymatic action of microorganisms may adversely affect the redox reaction. The transformation of the elements and the availability of nutrients in soil are also influenced by redox reactions. This paper mainly reviews the redox reaction in various aspects that are connected to pH relations, the response of microorganisms, its effect on soil fertility, nutrient availability, plant growth, and the response of plants due to the redox reaction, which are all positioned in the existing documents. Need more investigation to determine the individual factors contribution.

Keywords: Redox reaction, relations between pH and Eh, nutrient status, plant response to Eh, microorganism response to Eh.

INTRODUCTION

The combination of proton and electron transformations is the source of soil chemical reactions. If there is a loss of electron in the process of reaction, it tends to oxidation, while a gain of electron leads to reduction. The oxidation components, or oxidants, are generally called electron acceptors, while the reduced components, or reductants, are the electron donors. In a soil solution, the electrons are not in a free state, so both the oxidant and reductant must be in close contact. The simultaneous occurrence of both oxidation and reduction together denotes the redox (oxidation-reduction) reaction (Barden & James 1993). The transfer of electrons from one compound to another plays a major role in biological systems by regulating many reactions (Sjulstok *et al.*, 2015), and in the surface environment, redox reactions control many bio-geochemical reactions (Falkowski *et al.*, 2008). Oxidation and reduction reactions are commonly found in submerged or waterlogged soil where the moisture content shows high variation, affecting the aeration status of the soil (Sajedi *et al.*, 2012). This oxidation-reduction reaction is responsible for affecting or altering the chemistry of living organisms, including the transfer of electrons and the acid-base reaction (Dietz, 2003). The soil oxygenation status is estimated by measuring it directly by assessing the soil air composition, permeability of air, and porosity, including micro- and macro-diffusion, and by assessing the soil aeration status indirectly by evaluating hypoxia effects (Glinski and Stepniewski 1985). Other than these oxidation-reduction reactions, they play a crucial role in the process of nutrient absorption and serve as critical controls for the bioavailability, toxicity, reactivity, and mobility of the nutrient (Sigg, 2000).

The redox potential, or Eh, is referred to as a measure of electron activity or potential of the soil. It is also referred to as the measure of electron availability within the system (Kjaergaard, 2006), and it is measured in volts (V) and millivolts (mV). Eh itself is defined as the difference in voltage between a platinum electrode and the standard hydrogen electrode.

RANGE OF REDOX POTENTIAL (mV)

Kaurichev and Shishkova (1967) distinguished four main classes of soil in terms of oxidation and reduction conditions. well-drained soil with over 400 mV. moderately reduced soil with Eh ranging from 100 to 400 mV. Reduced soil Eh ranges from -100 to 100 mV. Highly reduced soil has a range of -300 to -100 mV.

Table 1: range of redox (oxidation and reduction) potentials encountered in rice soils ranging from well-drained to waterlogged conditions.

Soil water condition	Redox potential (mv)
Aerated or well drained	700 to 500
Moderately reduced	400 to 200
Reduced	100 to -100
Highly reduced	-100 to -300

Patrick and Reddy (1978)

SOIL pH AND EH RELATIONS

The redox potential (Eh) and the soil pH are characteristics of the temporal variability in a diurnal and seasonal cycle (Snakin *et al.,* 2001; Mansfeldt, 2003). The soil pH and oxidation-reduction reaction are the main factors that control the rate and intensity of the humidification process (Rusanov and Anilova 2009). In reduced soils, the pH range was more narrow (negative eh) than in oxidized soil (positive eh). Based on the results of Baas Becking *et al.* (1960), the soil is divided into three categories: normal (oxidized), wet (seasonally saturated), and waterlogged (semi permanently saturated).

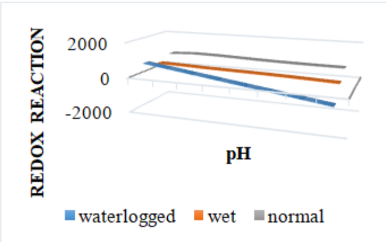


Fig. 1. Probability in variation of redox reaction (Eh) along with the pH.

The relationship can be expressed in terms of equilibrium constant K^0 (Patrick *et al.*, 1978).

$$\log K^0 = \log(\text{red}) - \log(\text{ox}) - n\log(e^-) - m\log(H^+)$$

The -log (e^-) was defined as pe in similar way as pH expressed. The pe is an intensity factor as it is an index of electrons at free energy level per mole of electrons (Ponnamperuma, 1972). It represents, thus, that pe and pH are considered master variables of a soil and must be known completely. Where ox is the oxidized compound, also known as the electron acceptor, red is the reduced compound, also called the electron donor, m is the number of hydrogen ions involved in the reaction, and n is the number of electrons involved in the reaction.

Table 2: Oxidation/Reduction potential of some reaction.

Reaction	Potential(v) at pH 7
Acetate Acetaldehyde	-0.60
Hydrogen – H^+	-0.42
66Glutathione(ox) glutathione(red)	-0.23
Acetaldehyde ethanol	-0.20
Pyruvate lactate	-0.19
$Fe(OH)_3$ Fe^{2+}	0.1
Cu^{2+} Cu^+	0.2
Oxygen H_2O	0.82

(Williams and Silva 2006)

In soil analysis pH is defined as Acid-base reaction. Highly reduced soils are less acidic and less alkaline in nature (Dayo-Olagbende *et al.,* 2022) compared to moderately reduced and oxidized soils. Therefore, the pH of acidic soil increases due to a decrease in redox potential (Dong *et al.*, 2014). In alkaline conditions, the redox potential is directly proportional to the pH, whereas in acidic conditions, the redox potential is inversely proportional to the pH (Dayo-Olagbende *et al.*, 2022). Observed (Sahrawat, 2007), changes in Eh and pH in submerged rice soil lead to the transformation and availability of major and micronutrients. It was found that the changes in redox reactions ultimately interrupted the microorganisms that are present in the soil; some may prefer an aerobic condition, and some microorganisms can live in anaerobic conditions of the soil. The oxidation and reduction reactions that determine and regulate the abundance and species diversity of microbial communities have been determined by many authors (Ludemann *et al.*, 2000; Pett-Ridge and Firestone 2005; Hines, 2006; Song *et al.*, 2008).

OXIDATION-REDUCTION REACTION EFFECTS ON MICROORGANISMS

In submerged soils, the electron acceptors by facultative and obligate anaerobic microorganisms after the disappearance of O_2 result in the reduction of several oxidized components. Microbes utilize several of these oxidized soil components and reduce the oxidation number of the oxidized atom, which is generally referred to as sequential reduction.

Table 3: Redox potential of major reduction process in soils.

Process	Electron acceptor	Redox potential (mV)
Oxic respiration	$O_2 \rightarrow CO_2$	500-600
Denitrification	$NO_3 \rightarrow N_2$	300-400
Fermentation	Organic compound	<300
Reduction	$Fe^{+3} \rightarrow Fe^{+2}$	200
Sulfate reduction	$SO \rightarrow H_2S$	-100
Methane production	$CO_2 \rightarrow CH_4$	-200

(Reddy *et al.*, 1986; Avnimelech *et al.*, 2003)

Growth of microorganisms are affect by redox potential. According to Kimbrough *et al.* (2006), the growth of the bacterial population was found to be directly related to changes in redox potential, whereas enzymatic activities were negatively correlated with oxidation and reduction reactions in anaerobic soil (Kralova *et al.,* 1992; Brzezinska, 2004). Soil microorganisms exhibited a higher capacity to modify or totally change the pH and redox potential of their environment to attain their requirements (Fierer and Jackson 2006). Probably the very first researcher denoted that the soil microorganisms utilizing oxygen as an electron acceptor in the respiratory chain lead to a decrease in the redox potential (Potter, 1911). The microbial population seems to be higher in neutrally conditioned soils and less in acidic conditions

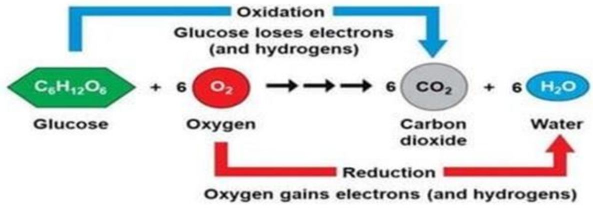
(Hinsinger *et al.,* 2009; Lauber *et al.,* 2009). Fluctuations of the redox potential are considered the major factor that determines the phylogeny and physiology of soil microorganisms, and changes in redox potential favour the flexibility of metabolism or mechanisms that enhance growth in a wide range of oxidation and reduction reactions (Ewelina Tokarz *et al.,* 2015). The bacteria that prefer an aerobic condition require a relatively higher value of redox potential for their growth and development (Rabotnova and Schwart 1962). According to the observation of Hibbing *et al.* (2010), *the* bacterial population develops a survival mechanism sometimes via the release of toxin into their environmental circle, which results in increasing the competition for oxygen, nutrients, and space (Amarasekare, 2002; Riedel *et al.*, 2013; Lloyd & Allen 2015). When the population becomes dense, it can cause the microbial population to drop. In the observation of Dayo-Olagbende *et al.* (2019), aerobic organisms responsible for carbohydrate breakdown formed glucose and released high energy. In reduced conditions, prevailing organisms can split glucose into two molecules of pyruvate, whereas in oxidized conditions, organisms can breakdown the glucose into carbon dioxide and emit it as a waste product during cellular respiration. This could represent the presence of more CO_2 in oxidized soils when compared with reduced or highly reduced soil. The soil type is responsible for microbial communities' particularly bacterial population (Garbeva *et al.,* 2004; Fang *et al.,* 2005). In addition to that, clay loam and silt clay loam had a greater growth in bacterial population than sandy loam (Najmuldeen, 2010). The reason is that sandy soils cannot hold water and are easily drained, while clay soils have greater nutrient and water-holding capacity. The increase in clay content in soil results in an increase in nutrient and water holding capacity, which leads to an increase in the bacterial population (Heritage *et al.,* 2003).

EFFECTS ON REDOX POTENTIAL ON SOIL FERTILITY AND NUTRIENT AVAILABILITY

Some elements are considered to be essential for plants to complete their lifecycles. The changes in redox conditions affect the transformation that occurs to these elements (Dayo-Olagbende *et al.,* 2022). In reduced conditions, the oxidized form of many substances is changed to a reduced form (Ojanuga *et al.,* 1996). Reduced and highly reduced soil induces changes in the oxidation state of nitrate (NO_3), reducing it to nitrous oxide (N_2O) or atmospheric nitrogen with the help of anaerobic organisms. The availability of nitrogen reduces once volatilization occurs. This could explain the low nitrogen content observed in reduced and highly reduced conditions. Nitrate is the major form of nitrogen in completely oxidized soil (Prosser, 2007). Whereas in waterlogged soils, the major form of nitrogen is (NH_4) ammonia (Prasad *et al*., 1986). Volatilization of ammonia is rare, and the net effect of waterlogging is the accumulation of ammonia (Philip and Greenway 2008). Nitrogen is highest under moderately reduced conditions because moderately reduced soil is an intermediary between oxidized and reduced; it contains oxygen with which nitrifying bacteria carry out their activities; all the compounds are not oxidized; and it allows for some accumulation of ammonia. As a result, it contains both nitrate and ammonia (Dayo-Olagbende *et al.,* 2022). Phosphorus has been found to exist in valence states from +3 to -3. It is highly reactive, so it is not found as a free element (Greenwood and Earnshaw 1996). In acidic conditions, phosphorus, in its oxidized form, can form complexes with iron oxides or aluminum oxides. In alkaline conditions, they are oxidized with calcium to form calcium phosphate (Stumm and Morgan 1981). In submerged soils, phosphorus is more stable in solutions, making their content on exchangeable sites reduce. According to this observation, phosphorus is low in reduced and highly reduced soil (Ojanuga *et al.*, 1996). Other than these elements, potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^+) are considered to be major. Positively charged of these elements in highly reduced conditions had the highest Ca, Mg, and Na results in increasing the activities of facultative anaerobes on other soil components with higher valence like iron (Fe^{3+}) and manganese (Mn^{2+}) (Dayo-olagbende *et al.*, 2022). In waterlogged conditions, the levels of Fe and Mg were increased, as stated by Lu *et al*. (2004).

BASIC PLANT RESPONSE TO Eh

Redox potential plays an important role in agriculture, as its effect directly creates an impact on yield during crop production. Redox potential influences plant growth. Plants show various tolerances to changing oxidation-reduction conditions and soil reactions (Ewelina Tokarz and Danuta Urban 2015). The root zone exhibits different oxidation and reduction conditions (Hartmann *et al.,* 2009). Uptake of nutrients is impaired in reducing conditions due to dysfunction of roots, and in severe conditions, roots become dead (Delaune *et al.,* 1998, 1999; Kogawara 2006). In some bottom-plant woody species, elongation of roots was inhibited when the soil Eh fell below 350 mV (Pezeshki *et al.,* 1990). Oxygen transport from plants to the atmosphere was more Eh-dependent, ranging from -250 mV to -150 mV (Stottmeister *et al.,* 2003). Under prolonged waterlogging, the pH and redox potential decreased, and the reduction of iron and magnesium led to an increase in the availability of these elements, resulting in a high level of these elements in plant tissues. The higher concentration of these elements was observed more in anaerobic plants than aerobic plants (Gries *et al.,* 1990). Reducing conditions affect the most fundamental processes of plants, including gas exchange, nutrient uptake, photosynthesis, phytohormonal balance, and biomass production (Ewelina Tokarz and Danuta Urban 2015). Wetland plant gas exchange and growth were highly influenced by soil Eh capacity (Kludze *et al.,* 1995).



$$6CO_2\ (g) + 6H_2O\ (l) \xrightarrow{\text{Light energy}} C_6H_{12}O_6\ (aq) + 6O_2\ (g)$$

From this equation, we determine which elements undergo oxidation and reduction by calculating their oxidation states.

In photosynthesis, there are two main reactions that take place. Light-dependent (occurs in the presence of light) and light-independent (does not require light). A light-dependent reaction is the first redox reaction.

$2H_2O + 2NADP^+ + 3ADP + 3P_I +$ Light $2NADPH + 2H^+ + 3ATP + O_2$

Here, oxygen is formed due to the oxidation of water by NADP+ and $NADP^+$ is reduced to NADPH by water. A light-independent reaction is the second redox reaction.

$3CO_2 + 9ATP + 6NADPH + 6H^+$

$C_3H_6O_3$-Phosphate $+ 9ATP + 8P_I + 6NADP^+ + 3H_2O$

Here, carbon dioxide is reduced by NADPH to form $C_3H_6O_3$-Phosphate, and NADPH is oxidized by carbon dioxide to form $NADP^+$ again. Plant response to low soil pH conditions requires the ability to utilize a variety of morphological, anatomical, and metabolic defense mechanisms. The tolerance and avoidance of such species with low soil redox conditions are negatively impacted (Pezeshki and DeLaune 2012).

CONCLUSIONS

The oxidation and reduction of the soil are major factors that influence nutrient availability, which directly affects plant survival, growth, and productivity (Pezeshki and DeLaune 2012). The presence or absence of soil microbes is determined by oxidation and reduction potential. The redox potential is greater than 100 mV (moderately reduced and oxidized), offering the microbes oxidation and reduction status of soil, whereas the redox reaction is less than 100 mV (reduced and highly reduced soil). The effect of soil texture is not significant and reduces oxidation and reduction status (Olufemi Gabriel Dayo-Olagbende, 2020). In soils with low organic matter, slowing down the reduction process results in less benefit in terms of soil fertility under submerged conditions (Sahrawat 1998; Narteh and Sahrawat 1999, 2000). Soil pH was greatly altered the soil condition due to the result of oxidation and reduction reaction. The oxidation process tends pH towards acidity or alkalinity; however, the reduction process tends pH towards a neutral condition (Dayo-Olagbende *et al.*, 2022).

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How to cite this article: Abirami R., S. Jothimani and D. Leninraja (2023). Mechanism of Redox Reaction in Soil Chemistry. *Biological Forum – An International Journal, 15*(10): 1317-1321.