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Biochar consequences on cations and anions of sandy soil

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Abstract

Natural and anthropogenic imbalance of cations and anions cause soil degradation. This is major concern of soil well being for cultivation. The imbalance of these ions adversely affects the nutrients bioavailability which leads towards less productivity. To evaluate ionic imbalance an incubation experiment was conducted using 3 levels of biochar (BC_0, BC_5 and BC_{15}) under tap water (TW) and sewage water (SW) irrigations in the NFC-IET University, Multan. Results indicated that BC significantly enhanced the concentration of ions in the sandy soil when incubated at 65% field capacity moisture under 35 °C for 40 days. Application of BC_{15} + SW significantly enhanced pH (4.2%) and TSS (5.1 folds) of sandy soil as compared to control biochar. In the same way BC_{15} addition also amplified the Ca^{+2}+ Mg^{+2} (4.2 folds) and Na^{+1} (5.4 folds) ions as well as HCO_3^{-1} (3.6 folds) and Cl^{-1} (33 folds) concentrations in soil. These HCO_3^{-1} ions might play a dynamic role in the extraction of exchangeable phosphorus. Higher Cl^{-1} ions may induced toxicity in the plants and restrict microbial activities as well in soil. SW irrigated biochar amended soil retained more water soluble ions as compared to the TW. Thus it is concluded that BC_{15} significantly increased SAR (2.6 folds) and RSC (1.84 folds) of sandy soil as compared to control biochar. That's why a BC having high Na^{+1} should be discouraged as reclaiming agent in saline and sodic soils.

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Introduction

Biochar (BC) is a black carbon soil conditioner that is continuously gaining the attention of scientists now a day due to its potential, benefits regarding ecologically soil restoration. The manufacturing of BC is done under limited supply of oxygen in pyrolyzer at high temperature through process of pyrolysis (Danish *et al.,* 2014). After pyrolysis, the waste biomass is changed into alkaline bio-oil component inherited from waste material used for BC production (Liu and Zhang, 2012). The pH of BC is dependent on the temperature of pyrolysis. At high temperature, BC usually become more alkaline as compared to the lower temperature (Mukherjee *et al.,* 2011). This alkalinity is provided by presence of organic and inorganic ions in biochar. The anions (chlorides, sulphates, carbonates and bicarbonates) presence in the soils also enhanced the soil salinity level, which disturb many biological activities (Tavakkoli *et al.,* 2011). Among cations, Ca^{+2} ions are rich part of BC through which BC modifies its liming affects (Yuan and Xu, 2011). Plants which are cultivated in the BC amended soils response better in growth through modifications in soil CEC and nutrients retention (Peng *et al.,* 2011). Higher contents of Ca^{+2}, Mg^{+2} and Na^{+1} are reported in the BC that provides these nutritional elements in the soil solution to regain fertility level (Amonette and Joseph, 2009). The release of anions (HCO_3^{-1}) in the BC directly affects the release of nutrients from soil. It is noted that more bicarbonates in the soil solution increase the extraction of exchangeable phosphorus (Chintala *et al.,* 2013). During incubation of soils it is evaluated that anions are quite easily released by BC as compared to original feedstock before their pyrolysis (Yuan *et al.,* 2011). Application of untreated sewage water as irrigation in the soils degrades soil physiochemical properties due to presence of overloaded ions (Cameron *et al.,* 1997). Higher application of sewage water and organic amendments having more Na can replace the Ca from the exchange sites (Pils *et al.,* 2007). Increasing exchangeable sodium percentage (ESP) in the soil after sewage water application resulted in declining the hydraulic conductivity of soil (Sumner, 1995). In previous studies scientists had worked on the immobilization of metals and bioavailability of nutrients (Uzma *et al.,* 2014) without focusing the biochar release anions that might affect nutrients mobilization or immobilization if applied in large amount. For understanding the ionic balance of different soils in the presence of various biochar rates a lot of work has to be done. For that purpose an incubation experiment was conducted to evaluate the potential release of water soluble Na^{+1} in the sandy soils along with anions (bicarbonates and chloride) that help in extraction of exchangeable phosphorus. Also to figure out the application rate of biochar that has positive effects without tremendously increasing SAR and RSC under sewage water and tap water irrigations.

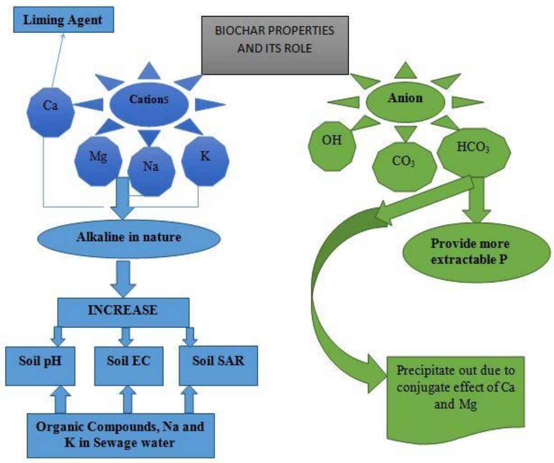

Fig. 1. Cotton sticks biochar consequences on cations and anions of sandy soil.

Materials and methods

Soil

An incubation experiment was conducted in NFC-IET University Multan by using sandy soil. The chemical characterization of sandy soil is provided in Table 1.

Biochar

Cotton sticks were collected from the local agricultural area and after air drying long sticks of cotton were pyrolyzed in a specially designed pyrolyzer at 411 ^{o}C in limited supply of oxygen. After the production of biochar (BC), it was grinded in the wheat grain grinder. At the end, BC was passed through 5 mm mesh (to get < 5 mm particle size) and packed in airtight packets (Danish *et al.,* 2014). The chemical characterization of biochar is provided in Table 2.

Table 1. Characterization of Soil.

Characteristics	Units	Values
pH (1:5)	-	7.21
EC (1:5)	dSm^{-1}	0.06
Total Soluble Salts	meq./L	0.62
Total Nitrogen	µg kg^{-1}	0.4
Total Phosphorus	µg kg^{-1}	0.9
Total Potassium	µg kg^{-1}	0.7
Water soluble Carbonates	µg kg^{-1}	0.00
Water soluble Bicarbonates	meq./L	0.25
Water soluble Chlorites	meq./L	0.01
Water soluble Sulphates	meq./L	0.36
Water soluble Ca^{+2} + Mg^{+2}	meq./L	0.23
Water soluble Sodium	meq./L	0.39
Sodium Absorption Ratio	meq./L	3.64
Residual Sodium Carbonate	meq./L	0.02

Table 2. Chemical characterization of cotton sticks biochar (BC).

Characteristics	Units	Values
pH (1:5)	-	8.21
EC (1:5)	dSm^{-1}	0.78
Total Soluble Salts	meq./L	7.80
Cation exchange capacity	$cmol_c$ kg^{-1}	33
Volatile Matter	%	34.89
Ash Content	%	41.69
Fix Carbon	%	23.42
Total Nitrogen	%	0.19
Total Phosphorus	%	1.89
Total Potassium	mg/kg	63
Water soluble Carbonates	meq./L	0.04
Water soluble Bicarbonates	meq./L	3.21
Water soluble Chlorites	meq./L	1.03
Water soluble Sulphates	meq./L	3.52
Water soluble Ca^{+2} + Mg^{+2}	meq./L	2.73
Water soluble Sodium	meq./L	5.07
Sodium Absorption Ratio	meq./L	4.33
Residual Sodium Carbonate	meq./L	0.48
Temperature	°C	411
Time	Min.	92
Size of particles	mm	<5

Water sources

Tap water (TW) was collected from the NEC-IET University (30° 13′ 13″ N, 71° 32′ 18″ E) while sewage water was collected from the NEC-IET boy's hostel sewage line. The chemical characteristics of tap water (TW) and sewage water (SW) are given in Table 3a and 3b.

Table 3a. Tap water chemical characterization.

Tap Water		
Characteristics	Units	Values
pH	-	7.86
EC	dSm^{-1}	0.77
Total Soluble Salts	meq./L	7.74
Water soluble Carbonates	meq./L	0.00
Water soluble Bicarbonates	meq./L	2.00
Water soluble Chlorites	meq./L	4.01
Water soluble Sulphates	meq./L	1.73
Water soluble Ca^{+2} + Mg^{+2}	meq./L	1.93
Water soluble Sodium	meq./L	5.81
Sodium Absorption Ratio	meq./L	5.92
Residual Sodium Carbonate	meq./L	0.07

Table 3b. Sewage water chemical characterization.

Tap Water		
Characteristics	Units	Values
pH	-	7.86
EC	dSm^{-1}	0.77
Total Soluble Salts	meq./L	7.74
Water soluble Carbonates	meq./L	0.00
Water soluble Bicarbonates	meq./L	2.00
Water soluble Chlorites	meq./L	4.01
Water soluble Sulphates	meq./L	1.73
Water soluble Ca^{+2} + Mg^{+2}	meq./L	1.93
Water soluble Sodium	meq./L	5.81
Sodium Absorption Ratio	meq./L	5.92
Residual Sodium Carbonate	meq./L	0.07

Jars Filling

The pre-weighted amounts of biochar (5 g and 15 g) and soil (0.5 kg) were mixed by hand initially and jars were filled. The moisture in the jars was maintained at 65 % FC throughout the experiment (40 days) through tap and sewage water. The temperature during the incubation was maintained 35 °C.

Chemical characterization of biochar

pH and EC of biochar (BC) was determined by following the methodology of Singh *et al.* (2010). Volatile matter (%) and Ash contents (%) were evaluated according to the Mclaughlin (2010) while CEC of BC was determined according to Richards (1954). Fixed carbon (%) was calculated using the equation of Noor *et al.* (2012)

FC (%) = 100 – (% Volatile matter + % Ash content)

Nutrients in water, soil and biochar

Nitrogen in the BC was done by H_2SO_4 digestion using catalyst mixture of K_2SO_4: $CuSO_4$: $FeSO_4$. After that the distillate was collected in H_3BO_3 and titration was done at pH 5.0 with dilute H_2SO_4 (Bremner and Mulvaney, 1982). Phosphorus of soil was determined according to the Olsen and Sommers (1982). BC phosphorus was analyzed by yellow color method on spectrophotometer. Potassium was analyzed on flame photometer by digesting the soil and biochar with HNO_3:$HClO_4$. Similarly, water sample was run on flame photometer to detect the potassium in wastewater after its filtration (Zarinkafsh, 1993). Water-soluble ions in biochar, water (TW and SW) and soil samples were determined by titration (APHA, 1998). Chloride was analyzed by following the methodology of Richards (1954).

Statistical Analysis

The data of water-soluble cations and anions were analyzed statistically by two way analysis of variance (ANOVA) using MS EXCEL. Turkey's Test was used to show significant ($P \le 0.05$) differences between treatments of biochar, tap water and sewage water.

Results and discussions

Soil pH

The results indicated that the main and interactive effects of biochar and irrigation were significant ($P \le 0.05$) on the pH of soil after 40 days of incubation at 35 °C at 65 % field capacity moisture (Table 4). Higher application rate of biochar (15g BC / 0.5kg soil) significantly ($P \le 0.05$) enhanced the sandy soil pH (1.13 folds) as compared to the control biochar (Table 4). SW application also significantly ($P \le 0.05$) increased the pH (11.3 %) in CB_0 treatment soil than that of TW (Table 4). However, an increase in the soil pH between CB_5 and CB_{15} was not significant (Table 4). Maximum value of soil pH (8.29) was noted in the CB_{15} + SW while minimum pH (7.29) was noted in CB_0 + TW treatment soil.

An increase in soil pH by increasing BC application rate might be due to the presence of alkali elements (Ca, Mg and Na) and the presence of OH ions in biochar. Yuan *et al.* (2011) also noted similar type of results on the soil pH when they applied the BC in their experiment as soil amendment. They argued that Ca, Mg and Na are the alkaline cations that make biochar alkaline. According to Novak *et al.* (2009) presence of –OH ions in the BC enhanced its pH and ultimately the soil in which biochar is applied (Bilgic and Caliskan, 2001). Wong and Swift (2003) suggested that decarboxylation of organic anions is the main reason alkaline nature in BC when it is produced at high temperature. Rusan (2007) also reported that when soils are irrigated with the sewage water their pH (Rattan *et al.,* 2005). According to Khai *et al.* (2008) initially the presence of organic compound in the sewage waters are decomposed in the soil caused decrease in soil pH but with the passage of time the alkaline ions in the sewage water modified soil pH (Vaseghi *et al.,* 2005).

Total Soluble Salts

The main and interactive effects of irrigation and biochar were significant ($P \le 0.05$) on the soil total soluble salts after 40 days of incubation at 35 °C at 65 % field capacity moisture (Table 4). However, an application of SW non-significantly ($P \le 0.05$) increased the TSS (2.09%) in CB_{15} as compared to the CB_0 treatment (Table 4). On an average increasing rate of biochar (BC_{15}) significantly ($P \le 0.05$) enhanced the TSS (6.4%) as compared to BC_0. However, CB_{15} non-significantly increased the TSS (2.5 %) as compared to the CB_5 (Table 4). Highest value of soil TSS (10.03 meq. / L) was noted in the CB_{15} + SW while least TSS value (1.10 meq. / L) was noted in CB_0 + TW. According to the Jahantigh (2008) high EC value of sewage water increased the soil EC. Khai *et al.* (2008) suggested that the presence of high concentration of K and Na ions in the sewage water increased the EC of water and their exchange in the soil solution enhanced EC of soil solution. Rusan *et al.* (2007) in their study also noted similar type of results when they applied sewage water as an irrigational source. Kordlaghari *et al.* (2013) found that the higher concentration of ions in the sewage water is the basic reason that increases EC of soil and total soluble salts. According to Lima and Marshall (2005) the release of Ca, K, Mg and Na ions by BC increases the EC of soil. They argued that BC releases these ions in the soil solution through ion exchange mechanism (Tyron, 1948). Similar sort of results were also found by the Yeboah *et al.* (2009) where BC addition decreases the loss of nutrients while nutrients ions retention enhanced soil EC.

Table 4. Effect of cotton sticks biochar (CB) on pH and total soluble salts of sandy soil under tap and sewage water.

Cotton sticks biochar (CB)	Tap Water (TW) and Sewage Water (SW)					
	TW	SW	Mean	TW	SW	Mean
	Soil pH			TSS (meq./L)		
CB_0 (0g/0.5Kg soil)	7.29b	8.12a	7.70B	1.10f	2.70e	1.90A
CB_5 (5g/0.5Kg soil)	7.90a	8.15a	8.02A	6.16d	8.40c	7.28B
CB_{15} (15g/0.5Kg soil)	8.11a	8.29a	8.20A	9.20b	10.03a	9.62C
	7.76B	8.18A		5.48B	7.05A	

The values followed by different letters along column are significantly different at $P \leq 0.05$.

Table 5. Effect of cotton sticks biochar (CB) on sodium absorption ratio (SAR) and residual sodium carbonates (RSC) of sandy soils under tap and sewage water.

Cotton sticks biochar (CB)	Tap Water (TW) and Sewage Water (SW)					
	TW	SW	Mean	TW	SW	Mean
	SAR (meq./L)			RSC (meq./L)		
CB_0 (0g/0.5Kg soil)	2.42b	3.05b	2.73B	0.02a	0.36a	0.19A
CB_5 (5g/0.5Kg soil)	6.45a	7.20a	6.82A	0.07a	0.53a	0.30A
CB_{15} (15g/0.5Kg soil)	7.01a	7.26a	7.13A	0.18a	0.51a	0.35A
	5.29B	5.83A		0.09B	0.47A	

The values followed by different letters along column are significantly different at $P \leq 0.05$.

Bicarbonate ions

The main effect of BC and irrigation was significant ($P \leq 0.05$) on the water-soluble bicarbonates release (Table 6). In comparison with TW + CB_0 soil irrigation of SW significantly ($P \leq 0.05$) increased the water-soluble bicarbonates up to 4.26 folds in CB_0. Similarly, SW application enhanced the water soluble bicarbonates 1.80 and 1.25 folds in CB_5 and CB_{15} respectively as compared to the CB_5 and CB_{15} having TW irrigation (Table 6). On an average SW significantly ($P \leq 0.05$) enhanced water soluble bicarbonates (65%) as compared to TW. However, highest application rate of BC_{15} significantly ($P \leq 0.05$) amplified water soluble bicarbonates ions (258%) as compared to control biochar (Table 6). However, water soluble bicarbonates were increased

45 % in CB_{15} in comparison with CB_5 (Table 6). According to Yuan *et al.* (2011) the alkaline nature of BC is developed when the Na, Ca and Mg ions in biochar react with carbonates and bicarbonates ions. These ions developed liming ability in biochar and make it preferable amendment for soil reclamation. Similar types of results were also noted by Novak *et al.* (2009) where formation of carbonates and bicarbonates ions enhances the BC alkalinity. In another study Chintala *et al.* (2013) noted that *Ponderosa pine* wood residues BC had higher bicarbonate ions that play a vital role in the extraction of soil phosphorus. In case of sewage water, Suarez *et al.* (2006) noted that sewage water irrigation enhanced the soil pH. They argued that this increase in the soil pH was due to high concentration of alkali ions. Similar type of results was also reported by Wu *et al.* (2008) where an increase in soil pH was resulted in precipitation of ions with bicarbonates in sewage water.

Table 6. Effect of cotton sticks biochar (CB) on bicarbonates and chlorides of sandy soil under tap and sewage water.

Cotton sticks biochar (CB)	Tap Water (TW) and Sewage Water (SW)					
	TW	SW	Mean	TW	SW	Mean
	HCO_3^{-1} (meq./L)			Cl^{-1} (meq./L)		
CB_0 (0g/0.5Kg soil)	0.27d	1.15c	0.71C	0.02d	0.05d	0.03C
CB_5 (5g/0.5Kg soil)	1.25c	2.26b	1.75B	0.62c	0.85b	0.73B
CB_{15} (15g/0.5Kg soil)	2.25b	2.83a	2.54A	0.89b	1.08a	0.98A
	1.26B	2.08A		0.51B	0.66A	

The values followed by different letters along column are significantly different at $P \leq 0.05$.

Chloride ions

Increasing rate of BC enhanced the water soluble Cl^{-1} significantly ($P \leq 0.05$) in the sandy soil as well as SW application in comparison with TW irrigation (Table 6). Soil which was amended with BC_{15}, contained 21.6 folds more water soluble Cl^{-1} as compared to BC_0 soil irrigated with SW. In case of TW + CB_{15} amended soil 44.5 folds higher water soluble Cl^{-1} were present in comparison to CB_0. An increment in water-soluble Cl^{-1} was non-significant (2.5 folds) where TW and SW irrigation was used as an irrigation. However, in CB_5 and CB_{15} under SW significant ($P \leq 0.05$) enhancement of 1.37 and 1.21 folds in water-soluble Cl^{-1} was noted as compared to TW irrigated soils. Najafi and Nasr (2009) reported that the sewage water application in the soil enhanced the concentration of chloride ions. They suggested that the dissolved minerals in the sewage are major contributor of the chloride ions. Similar sort of results were also reported by the Mojiri *et al.* (2011) during their study on sewage water influences on soil physiochemical properties.

Calcium and Magnesium ions

An application of SW significantly ($P \leq 0.05$) enhanced Ca^{+2} + Mg^{+2} as compared to the TW (Table 7). Similarly an increasing BC application rate (0 - 15 g BC / 0.5 kg soil) significantly ($P \leq 0.05$) increased the water soluble Ca^{+2} + Mg^{+2} in the sandy soils (Table 7). On an average SW, irrigated soils contained 37.6 % more of water soluble Ca^{+2} + Mg^{+2} as compared to TW. Similarly BC_{15} significantly ($P \leq 0.05$) increased (4.21 folds) the water soluble Ca^{+2} + Mg^{+2} in comparison to BC_0 amended soils (Table 7). The minimum water soluble Ca^{+2} + Mg^{+2} (0.25 meq./L) was noted in the CB_0 + TW treatment soil while maximum (2.31 meq./L) was noted in CB_{15} + SW soil (Table 7). Joseph *et al.* (2010) found that when the volatile matter is removed from the BC then the rest biomass of biochar contains a sufficient amount of Ca, Mg and inorganic ions in it that become the part of ash contents. Novotny *et al.* (2009) also reported that the terra preta soils, which were previously amended by BC, have higher Ca and Mg contents as compared to the non-BC amended soils. Shenbagavalli and Mahimairaja (2012) reported the presence of Ca and Mg ions in the BC at sufficient level that can make BC a liming agent. However, Suarez *et al.* (2006) related the presence of Ca and Mg in sewage water in precipitated form with bicarbonates.

Table 7. Effect of cotton sticks biochar (CB) on calcium + magnesium and sodium ions of sandy soil under tap and sewage water.

Cotton sticks biochar (CB)	Tap Water (TW) and Sewage Water (SW)					
	TW	SW	Mean	TW	SW	Mean
	Ca^{+2} + Mg^{+2} (meq./L)			Na^{+1} (meq./L)		
CB_0 (0g/0.5Kg soil)	0.25e	0.79d	0.52C	0.85e	1.91d	1.38C
CB_5 (5g/0.5Kg soil)	1.19c	1.73b	1.46B	4.97c	6.68b	5.82B
CB_{15} (15g/0.5Kg soil)	2.07ab	2.31a	2.19A	7.13b	7.72a	7.42A
	1.17B	1.61A		4.32B	5.44A	

The values followed by different letters along column are significantly different at $P \leq 0.05$

Sodium ions

The release of water-soluble Na^{+1} in the sandy soils was significantly ($P \leq 0.05$) high where SW was applied as compared to the TW. The soils having the treatment of CB_{15} + SW contained 8.27 % more water-soluble Na^{+1} as compared to CB_{15} + TW (Table 7). On an average SW enhanced 29 % water soluble Na^{+1} as compared to TW while 32.6 folds by CB_{15} and 24.3 folds by CB_5 than that of CB_0 (Table 7). According to Amonette and Joseph (2009) the BC contains significant proportion of calcium (Ca), magnesium (Mg) and sodium (Na) that become the part of soil solution through ion exchange mechanism. Similarly, Najafi and Nasr (2009) reported high concentration of Na ions in the sewage water as well. They attributed higher Na level as the presence of inorganic dissolved minerals in sewage water. Stumm and Morgan (1996) also reported same kind of results in which they found high Na ions in the sewage water increased soil sodicity.

Sodium Absorption Ratio

The main effect of BC and irrigation was significant ($P \leq 0.05$) on the SAR of soil. However an interactive of BC and irrigation (BC x I) was non-significant on both SAR and RSC of sandy soil (Table 5). The value of SAR was enhanced (138%) in the soils having treatment of BC_{15} + SW as compared to the BC_0 + SW. Similarly, an increment of 189.6% in the value of SAR was noted in the BC_{15} + TW as compared to the BC_0 + TW (Table 5). On an average, SAR was 10.2 % higher in the SW irrigated soil than TW. The maximum value of SAR (7.26 meq. /L) was noted in the BC_{15} + SW while lowest (2.42 meq./L) was recorded in BC_0 + TW (Table 5). The Suarez *et al.* (2008) also found an increase in the SAR of soil when they applied the sewage water as an irrigational source for the cultivation of crops. They suggested that this increase in the SAR of soil was due to presence of more Na and K ions in the sewage water that directly affect the soil infiltration rate (Murray and Grant, 2007). Presence of this high Na concentration increase soil dispersion that adversely affects soil structure. Also an increase in Na ions can cause the sodicity problems if continuously used for irrigation.

Residual Sodium Carbonates

On the RSC of soil the main effect of irrigation water was significant ($P \leq 0.05$) while BC main and interactive effects with irrigation (BC x I) were non-significant. Results indicated that an increasing rate of BC increased the RSC of soil non-significantly (Table 5). However, the SW significantly ($P \leq 0.05$) enhanced the RSC of sandy soils. In CB_{15} soil amendment application of SW amplified (2.83 folds) RSC than TW irrigated soil (Table 5). On an average 422 % increment in the RSC of soil was found when soil was irrigated with SW than that of TW. However, BC increasing rate enhanced the 84 % RSC on an average in BC_{15} + SW as compared to BC_0 + TW (Table 5). Shenbagavalli and Mahimairaja (2012) during their study on the characterization and effects of nitrogen and carbon dynamics in soil by BC noted that BC is also an important source of Ca^{+2} and Mg^{+2}. They found 11 g / kg Ca^{+2} and 0.36 g / kg of Mg^{+2} in the *prosopis* biomass produced BC. Due to high Ca^{+2} ions BC behaves like liming agent in the soil. According to the Suarez *et al.* (2006) presence of Ca^{+2} and Mg^{+2} ions in the waste water acts as conjugate ions that take part in the process of precipitation when high carbonates and bicarbonates ions are present. In that way bicarbonate, ions not only enhance their concentration but also bring more Ca^{+2} and Mg^{+2} along them.

Conclusion

Application of alkaline nature BC @ high rates in the soil along with sewage water can enhance the bicarbonates, chloride and sodium ions concentration. These bicarbonates ions play major role in phosphorous extraction as well as Ca^{+2} and Mg^{+2} precipitations in soil. In addition, the higher concentration of Na^{+1} can change the saline soils into sodic. So for long term modifications in the soils such BC should be recommended for sustaining the soil fertility that must have less water soluble Na^{+1} especially when prevailing conditions are saline or sodic. However, potassium absorption ratio (PAR) may become a key factor that can play a vital role in sustaining the soil physiochemical characteristics especially in the sodic soils.

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