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# Effects of biochar and modified biochar on Chromium contaminated soil properties

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***Abstract-*** **In recent years, increasingly more soils are getting contaminated with organic and inorganic toxins globally due to waste emissions. Among inorganic pollutants, heavy metals like carcinogenic chromium (Cr) are alarming to our environment, even though its environmental management is also ignored. As a result, Cr accumulates in plant tissues at toxic concentrations and ends up in the food chain. Therefore, pot experiments were conducted to investigate the effects of biochar and modified biochar application on the properties of Cr polluted soils and interaction of Cr with other soil nutrients. Two different biochar viz. rice stubble and saw dust were slowly pyrolyzed (450 ± 50ºC) and modified with 1*M* KOH. All biochars were applied at a rate of 20 t ha$^{-1}$ on soils artificially polluted with Cr at the levels of 0, 100, 200 and 300 µg g$^{-1}$. The biochars and modified biochars had significant effects (*P*<0.05) on available K, P, CEC, EC, and N of incubated soils. Therefore, it has convincing evidence that application of biochar and modified biochar is very imperative to improve soil health, ameliorate Cr polluted soils, reduce the amount of carbon produced due to biomass burning and thereby enhances plant growth.**

***Keywords-*** Biochars, Cr contamination, Cr remediation, modified biochars, physicochemical properties, soil properties.

## I. INTRODUCTION

SOIL is a critical life-support system of planet Earth, which supports essential ecosystem services such as biodiversity, biogeochemical cycling, and water cycling. Apart from this soil is still a fundamental resource of production for agriculture [1-5]. Contamination of soil by organic and inorganic pollutants has become a global concern for the last couple of decades. The greatest problems most likely involve Cr, Cd, Hg, Pb, As, Ni, Cu, Mo etc. to a greater or lesser degree and all these are also toxic. They are posing great threats to humans and ecosystems [6-7]. Heavy metals are naturally occurring in very low concentrations in soil but might become highly concentrated by human activities like mining, industrial production, bio solid and manure application, wastewater irrigation and inadequate management of agrochemicals are making the problem even more critical [8-9]. Climbing up the food chain, heavy metals can have various carcinogenic, teratogenic, and mutagenic effects on the human body. Among heavy metals chromium is a very carcinogenic and well-known primary pollutant and widely used in various industrial processes such as leather tanning, electroplating, timber treatment, petroleum, steelmaking, corrosion control and wood preservative. Chromate concentration in soils of Bangladesh is increasing alarmingly due to uncontrolled dumping of waste from industries specifically from leather industry, wood and paper processing, petroleum, mining and metal alloy production, paint manufacturing and corrosion control [11-15]. However, it is reported as high as 2800 mg kg$^{-1}$ Cr within 1 km of the wastewater and waste disposal site of Dhaka, Bangladesh, where maximum concentration of Cr is allowable 100 mg kg$^{-1}$ [11-13, 15].

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Biochar is a carbon rich recalcitrant product of biomass material which is produced by the slow thermochemical pyrolysis process under high-temperature and low oxygen condition. Biochar, being an alkaline and stable organic amendment to soil has many positive effects on soil nutrient availability, C sequestration, microbial community, and greenhouse gas emissions [16]. Besides the persistent characteristics of the biochar ensure long-term benefits for the amended soils. Biochar amendment to the soil proved to be beneficial as it increases nutrient use efficiency, water holding capacity [17-22], improves soil quality and thereby enhances plant growth [19-22]. Biochar application also improves the overall sorption ability of soils and therefore it might influence the toxicity, transport, and fate of different heavy metals in the soil. Biochar's potential can be greatly enhanced by modifying them with simple treatments. Modification can be done with several treatments like physical, chemical, or magnetic treatments. Resulting biochars should have increased surface area and surface functional groups than that of unmodified biochars [23-26]. Biochar amendment has been reported to improve soil physical and chemical characteristics and promoting pentachlorophenol decomposition [13-15].

Moreover, Impregnation with mineral oxides/ hydroxides is getting huge attention recently. Numerous studies have found that biochar application can decrease mobility, bioavailability, and toxicity of heavy metals in contaminated soils and thus reduce their uptakes by plants [14-15, 26]. We assume that KOH modified biochar will have better surface functionality than unmodified biochar. However, very few studies have been conducted about the influence of biochar and modified biochar application on the properties of chromium polluted soils. Therefore, the aim of the present study was to assess the effects of biochar and modified biochar application on the properties of chromium polluted soils.

# II. MATERIALS AND METHODS

Uncontaminated surface soil (0 to 15 cm) was collected from an agricultural field of Gopalpur thana of Tangail district, using composite soil sampling method [27]. The geographical location of the sampling site is $24^{0}62'85.8'$ North latitude, $89^{0}85'28.5''$ East longitude (Fig. 1). The elevation of the site is approximately 14 meters from sea level. The collected soil sample stood for the Sonatola series to Brahmaputra alluvium.

Soil samples were dried in the air and ground to pass through a 2 mm stainless steel sieve. Feedstocks for biochar production were selected depending on their availability and handy throughout Bangladesh. Two different feedstock samples were used in this study; saw dusts (SD) were collected from sawmill (Malek Timber and Sawmill) from Mohadebpur, Naogaon. Rice stubbles (RS) (Rice husk+ Rice straw) were collected from a local farmer of Kalushoher village, Mohadebpur, Naogaon (Table 1).

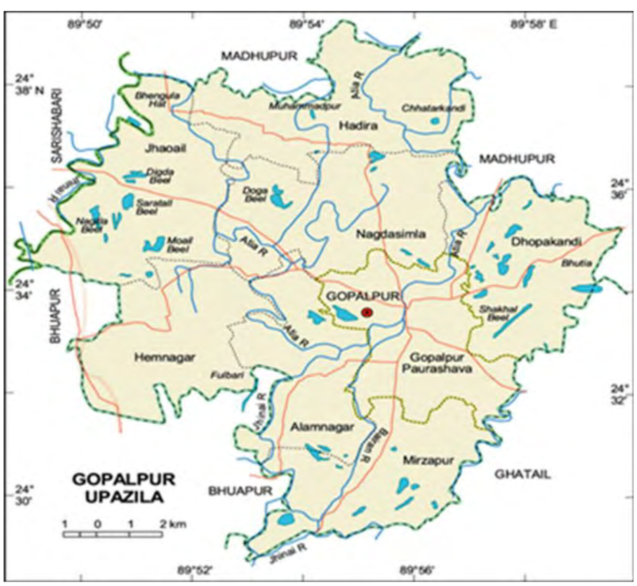


**Fig. 1.** Soil sampling site.

TABLE I

SYMBOLS USED FOR FEEDSTOCKS, BIOCHARS, AND MODIFIED BIOCHARS.

| Feedstocks | Biochars | Modified biochars |
|---|---|---|
| Saw Dust | Saw Dust (SDB) | Modified Saw Dust (SDB-M) |
| Rice Stubble (rice straw+rice husk) | Rice Stubble (RSB) | Modified Rice Stubble (RSB-M) |

## *2.1. Processing and Production of Biochar*

Before biochar production, all feedstocks were air dried under the sunlight for few days. After drying properly feedstocks were processed and pyrolyzed in a specially designed kiln. A specially designed kiln was made with a waste pressure cooker, stainless steel pipe and heat resistance rubber. The pipe was attached in the upper part of the cooker and the whole pressure cooker was made air tightened by the heat resistant rubber in the head of the cooker. The pipe was used to remove the syngas that produced in the cooker. Individual feedstocks were placed in the cooker and then the head of the cooker is locked in such a way that no oxygen can enter inside it. The cooker was then placed on the gas stover for burning. Approximate 450-500$^{0}$C was kept after one hour. The feedstocks were burnt for 3.5 hours keeping the above-mentioned temperature. After completion of the process, the cooker was removed from the stover and kept on the floor to cool down. After the biochar cooled down, the lid of the pot opened and screened through a 0.50 mm and 0.25 mm stainless sieve and then kept in plastic jars with paper tags showing source.

TABLE 2

TREATMENT COMBINATION

| Rate of biochar (t ha$^{-1}$) | Cr treatment (μg g$^{-1}$) | Arrangement of experiments | Labeling on pots |
|---|---|---|---|
| 0 | 0 | Soil+Fertilizer+$Cr_0$ | $Cr_0$C |
| | 100 | Soil+Fertilizer+$Cr_{100}$ | $Cr_{100}$C |
| | 200 | Soil+Fertilizer+$Cr_{200}$ | $Cr_{200}$C |
| | 300 | Soil+Fertilizer+$Cr_{300}$ | $Cr_{300}$C |
| 20 | 0 | Soil+Fertilizer+Biochar (Saw dust) + $Cr_0$ | $Cr_0$SDB |
| | | Soil+Fertilizer+Biochar (Saw dust modified) + $Cr_0$ | $Cr_0$SDB-M |
| | | Soil+Fertilizer+Biochar (Rice stubble) + $Cr_0$ | $Cr_0$RSB |
| | | Soil+Fertilizer+Biochar (Rice stubble modified) + $Cr_0$ | $Cr_0$RSB-M |
| | 100 | Soil+Fertilizer+Biochar (Saw dust) + $Cr_{100}$ | $Cr_{100}$SDB |
| | | Soil+Fertilizer+Biochar (Saw dust modified) + $Cr_{100}$ | $Cr_{100}$SDB-M |
| | | Soil+Fertilizer+Biochar (Rice stubble) + $Cr_{100}$ | $Cr_{100}$RSB |
| | | Soil+Fertilizer+Biochar (Rice stubble modified)+$Cr_{100}$ | $Cr_{100}$RSB-M |
| | 200 | Soil+Fertilizer+Biochar (Saw dust) + $Cr_{200}$ | $Cr_{200}$SDB |
| | | Soil+Fertilizer+Biochar (Saw dust modified) + $Cr_{200}$ | $Cr_{200}$SDB-M |
| | | Soil+Fertilizer+Biochar (Rice stubble) + $Cr_{200}$ | $Cr_{200}$RSB |
| | | Soil+Fertilizer+Biochar (Rice stubble modified)+$Cr_{200}$ | $Cr_{200}$RSB-M |
| | 300 | Soil+Fertilizer+Biochar (Saw dust)+$Cr_{300}$ | $Cr_{300}$SDB |
| | | Soil+Fertilizer+Biochar (Saw dust modified)+$Cr_{300}$ | $Cr_{300}$SDB-M |
| | | Soil+Fertilizer+Biochar (Rice stubble)+$Cr_{300}$ | $Cr_{300}$RSB |
| | | Soil+Fertilizer+Biochar (Rice stubble modified)+$Cr_{300}$ | $Cr_{300}$RSB-M |

After production biochars were further treated with 1M KOH in a ratio of 1:10 at 60-75$^0$C for 1 hr with continuous stirring [28]. After treatment modified biochars were allowed to cool down and their pH was adjusted around 7 with deionized water. Then the biochars were oven dried at 80$^0$C for 12 hrs.

### *2.3. Experimental Setup*

The experimental soil was incubated with these 4 biochars, fertilizer and different doses of Cr6+ which are 0 µg $g^{-1}$, 100 µg $g^{-1}$, 200 µg $g^{-1}$ and 300 µg $g^{-1}$. Fertilizer was given in a rate as recommended in the Soil Resources Development Institute (SRDI) online fertilizer recommendation system for Bangladesh Rice Research Institute (BRRI) [29].

### *2.4. Experimental Design*

Treatment combination and Cr reduction are as follows (Table 2). About 76 small sun antic pots were collected from the local market, cleaned properly, air-dried and labeled properly for the experimental setup. Each pot received 200 g of soil with treatment of biochar, fertilizers, and Cr doses. All pots were used to figure out the effect of biochar on nutrient availability in alternate field and submerged conditions. At first, all pots were kept in the laboratory in an orderly manner at a place where sunlight reaches for almost 2 hours each day. Then, those were re-arranged following randomization technique for each week. All pots were repeatedly checked every three days and 3 cm water above soil was kept for 3 months within 15 days field condition after 1.5 month.

### *2.5. Laboratory Analysis and Analytical Procedure*

The pH, electrical conductivity (1: 10 ratio), water holding capacity and cation exchange capacity (CEC) of biochar samples were measured [30]. Organic carbon of the feedstock and biochar was determined by the wet oxidation method [31]. Total N was determined by the Kjeldahl distillation method [32]. The concentration of P, K, and S in feedstocks and biochars were analyzed after digestion with nitric-perchloric acid [32]. Total P was measured colorimetrically using a spectrophotometer by developing yellow color with vanadomolybdate, total K by flame photometer, and total S by the turbidimetric method using a spectrophotometer [32]. The available nitrogen fraction was leached with 1N KCl solution. The nitrate ammonia was determined by reducing the nitrate to ammonia by suitable reducing agent (i.e., Devarda's alloy) in 40% and then ammonia formed from nitrate N was determined by alkali distillation [32]. Available P was extracted by Bray and Curtz [33] and Olsen [34] method. The extract was estimated by colorimetric method following the blue color method using Ascorbic acid [35] using spectrophotometer. The available K was estimated by the flame photometer [36]. The available S content of soil samples was determined by turbidity of suspended barium sulphate using Tween- 80 stabilizer after extracting with calcium di-hydrogen phosphate [Ca ($H_2PO_4$)] extractant solution and the turbidity was measured by spectrophotometer [37]. Statistical analyses were done by using Microsoft Excel 2010 and SPSS version 19.

## III. RESULTS AND DISCUSSIONS

### *3.1. Physical and Chemical Properties of the Soils*

Physicochemical properties of biochars and modified biochars are presented in Table 3.

TABLE 3
CHARACTERISTICS OF SOIL, BIOCHARS AND MODIFIED BIOCHARS.

| Parameters | Samples | | | | |
|---|---|---|---|---|---|
| | Soil | SDB | SDB-M | RSB | RSB-M |
| pH | 6.02±0.02 | 7.62±0.05 | 7.48±0.03 | 8.60±0.04 | 7.72±0.01 |
| EC (mS $cm^{-1}$) | 0.03±0.01 | 0.53±0.01 | 17.29±0.19 | 0.87±0.02 | 17.94±0.14 |
| CEC ($Cmol_c$ $kg^{-1}$) | 5.00±0.05 | 23.33±1.60 | 33.33±1.44 | 32.50±2.50 | 39.17±1.52 |
| OC (%) | 1.11±0.07 | 11.80±0.41 | 12.83± 0.0 | 12.32±0.41 | 23.97± 0.31 |
| N (%) | 0.0002±0.0001 | 0.47±0.02 | 0.39±0.02 | 3.04±0.18 | 2.84±0.35 |
| P (%) | 0.19±0.03 | 0.21±0.03 | 0.07±0.01 | 0.59±0.05 | 0.50±0.02 |
| K (%) | 0.02±0.01 | 0.36±0.04 | 5.90±0.90 | 0.58±0.07 | 6.07±0.80 |
| S (%) | 1.21±0.04 | 0.71±0.08 | 0.62±0.01 | 0.39±0.02 | 0.24±0.01 |
| Cr (µg $g^{-1}$) | 0.28±0.01 | 0.06±0.02 | 0.04±0.01 | 0.32±0.06 | 0.30±0.03 |
| PS (µ$m^2$) | - | 0.11±0.01 | 0.25±0.04 | 0.24±0.03 | 0.42±0.01 |
| SA (%) | - | 8.91±0.41 | 14.19±0.81 | 13.65±0.50 | 27.15±1.44 |
| *WHC (%) | 60.2±1.08 | 164.47±2.11 | 263.16±1.5 | 197.36±1.14 | 394.74±2.50 |
| Textural class | Silt loam | - | - | - | - |
| Total Ca (%) | 0.0003±0.00 | 0.49±0.04 | 0.29±0.01 | 1.85±0.02 | 1.53±0.01 |
| Total Mg (%) | 0.22±0.02 | 0.11±0.00 | 0.07±0.01 | 0.28±0.01 | 0.19±0.03 |

*WHC: Water holding capacity

### *3.2. Effect of Biochar, Modified Biochar and Incubation days on Cr Contaminated Soil pH, Organic C, CEC, EC, and Nutrient Availability*

#### *3.2.1. Effects on soil pH*

The soil reaction of all the treatments was recorded in every 30 days interval up to 90 days. Soil responded differently in terms of pH change after the first 30 days of incubation. At first pH of the soil increased and it was relatively neutral. From 60 days, soil pH started to decrease but there was an exceptional increase in the case of Cr300SDB and Cr200SDB-M treatments after 90 days (Fig. 2). Several research [38-39] suggested that alkaline biochar may increase the pH of acidic soil and it also showed a change in pH of acidic soil to a more neutral pH [40]. The initial pH increase in the first 30 days may be due to biochar's cation content and the effect of submergence. However, when with a higher pH value biochars are applied to the soil, the amended soil generally became less acidic [31]. The ANOVA result proved that incubation days have significant ($P<0.05$) impact on pH change neither have biochar treatments nor Cr dose. Least Significant Difference (LSD) at 5% level showed that soil pH under SDB and SDB-M treatments did not differ significantly from each other and control. Soil pH at different incubation days differ significantly from 0 incubation day and each other except 60 days from 90 days at 5% LSD level. Soil pH with different Cr6+ doses 100 µg $g^{-1}$, 200 µg $g^{-1}$ and 300 µg $g^{-1}$ did not differ significantly from each other and control 0 µg $g^{-1}$. The effect of rice stubble and modified rice stubble with recommended fertilizer dose (Fig. 3). From 0 to 90 days the results were recorded after every 30 days interval. However, application of rice stubble and modified rice stubble pH of the submerged soil increased after 30 days but there was gradual decrease from 60 to 90 days (Fig. 3). After a first stage of biochar addition, the soil pH could decrease to some extent due to formation of soluble carbonates by cations which could reduce hydroxyl content in soil [41]. However, pH of all incubated soil increased from the first soil pH 6.02. The biochar addition to the soil has also shown the increase in availability of basic cations and pH increase in earlier studies [42].

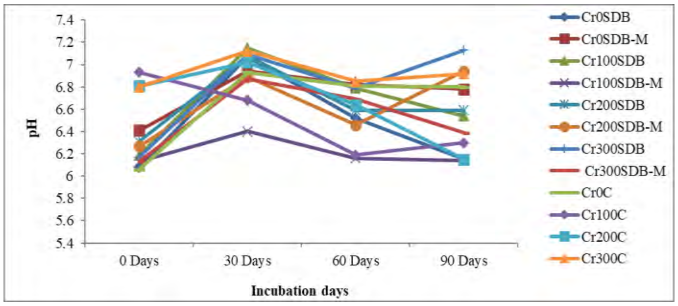


**Fig. 2:** Effect of sawdust & modified sawdust biochar application on soil pH.

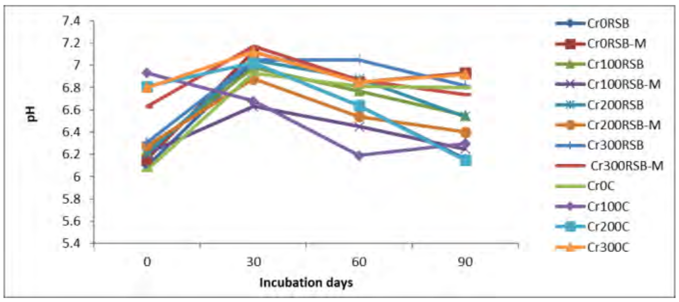


**Fig. 3:** Effect of rice stubble biochar & modified rice stubble biochar application on soil pH.

The application of biochar treatments and chromium dose did not significantly change the soil pH value, but the incubation period did at 5% significant level (P<0.05). LSD at 5% level showed that soil pH under RSB and RSB-M treatments did not differ significantly from each other and control. Soil pH at different incubation days differ significantly from 0 incubation day and each other except 60 days and 0 day from 90 days at 5% LSD level. Soil pH under different Cr6+ doses 100 µg $g^{-1}$, 200 µg $g^{-1}$ and 300 µg $g^{-1}$ did not differ significantly from each other and control 0 µg $g^{-1}$ except 100 µg $g^{-1}$ from 300 µg $g^{-1}$ at 5% LSD level.

### *3.2.2. Effects on soil organic carbon*

After the application of biochars organic carbon of soil consistently decreased with time up to 60 days, did not follow a sequential trend and started increasing for 90 days incubation except Cr300SDB (Fig. 4).

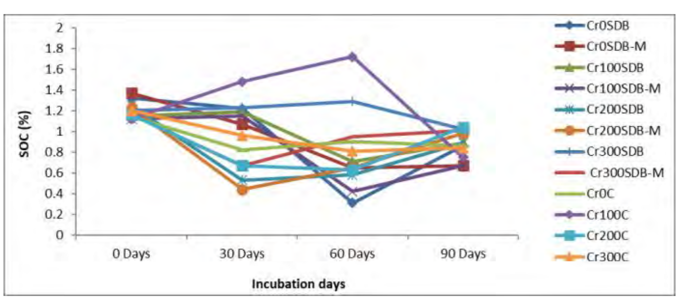


**Fig. 4:** Effect of sawdust biochar and modified sawdust biochar application on SOC (%).

The decreasing SOC could be due to the accelerated decomposition rate of the organic carbon by microorganisms after application of fresh biochar and assumed that it is still under speculation and calls for further investigation whether biochar application stabilizes soil OM and soil C, or results in priming [38-39; 43]. Incubation days significantly affected organic carbon content (*P*<0.05) but the treatments and Cr dose had an insignificant effect on soil organic carbon. LSD at 5% level showed that soil OC under SDB and SDB-M treatments did not differ significantly from each other and control. Soil OC at different incubation days differ significantly from 0 incubation day but not from each other at 5% LSD level. Soil pH with different Cr6+ doses 0 µg $g^{-1}$, doses 100 µg $g^{-1}$, 200 µg $g^{-1}$ and 300 µg $g^{-1}$ did not differ significantly from each other at 5% LSD level. The soil organic carbon (SOC) content of rice stubble and modified rice stubble amended soil samples at different incubation period is recorded (Fig. 4). The SOC content of incubated soil increased instantly but decreased for 30 days and 60 days, but it started increasing after 90 days.

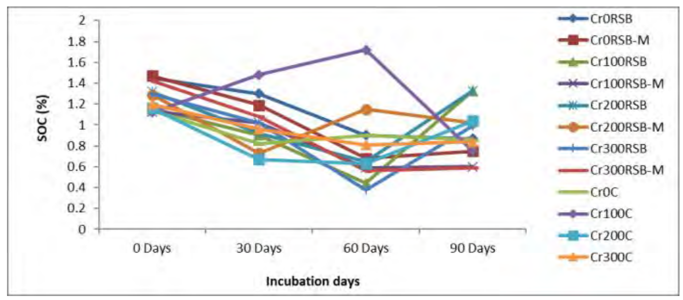


**Fig. 5:** Effect of rice stubble biochar & modified rice stubble biochar application on SOC.

The increase in organic carbon for 90 days incubation might be due to the increase in soil microbial biomass carbon after submergence and nutrient release of applied biochar [44]. Incubation days of submergence significantly changed soil organic carbon (*P*<0.05; Fig. 5). Biochar treatments along with chromium dose did not have any significant effect on organic carbon content of soil. Least Significant Difference at 5% level showed that soil OC under RSB and RSB-M treatments did not differ significantly from each other and control. Soil OC at different incubation days differ significantly from 0 incubation day except 60 days and 30 days from 90 days at 5% LSD level. Soil OC at different Cr6+ doses 0 µg $g^{-1}$, doses 100 µg $g^{-1}$, 200 µg $g^{-1}$ and 300 µg $g^{-1}$ did not differ significantly from each other at 5% LSD level.

### *3.2.3. Effects on soil cation exchange capacity (CEC)*

Soils amended with saw dust and modified saw dust biochar responded severally. Cation exchange capacity of 30 days incubated soils increased (Fig. 6) from the first value of soil 5.00 Cmolc $kg^{-1}$ except Cr100SDB (4.50 Cmolc $kg^{-1}$) and Cr300SDB (4.33 Cmolc $kg^{-1}$). There was a gradual decrease of CEC in soils of 60 incubation periods except Cr100SDB-M (7.50 Cmolc $kg^{-1}$), Cr200SDB-M (6.50 Cmolc $kg^{-1}$), Cr200SDB-M (7.00 Cmolc $kg^{-1}$). During the 3rd sampling CEC of the incubated soils responded differently. The CEC of some soils decreased, and some increased at the same time.

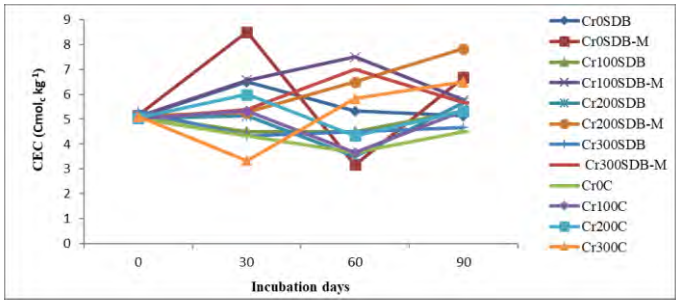


**Fig. 6:** Effect of sawdust biochar and modified sawdust biochar application on soil CEC (Cmol$_c$ kg$^{-1}$).

The CEC of 30 incubation days increased substantially due to pH change of soil. With addition of biochar, pH of the soil increased from acidic to alkaline. Alkaline pH increases amount of –OH functional group and submergence decreases decomposition of organic matter of soil as a result CEC increases. As biochar has organic matter and nutrients, its addition increased the CEC but with decrease of pH because of submergence and increasing incubation days CEC decreases. The soil CEC is changed significantly ($P$<0.05) through the effects of biochar treatments (Fig. 6).

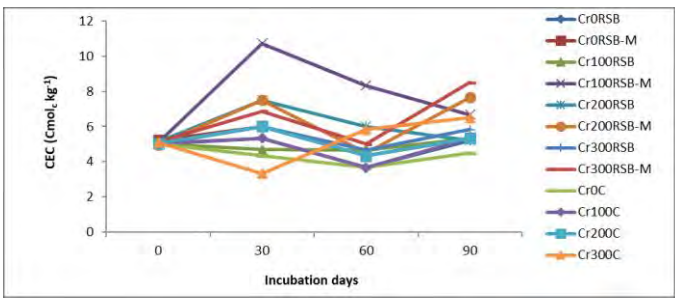


**Fig. 7:** Effect of rice stubble biochar and modified rice stubble biochar application on soil CEC (Cmol$_c$ kg$^{-1}$).

Incubation days and Cr doses did not affect CEC. The LSD showed that soil CEC under SDB and SDB-M treatments differed significantly from each other and control except SDB from control. Soil CEC at different incubation days did not differ significantly from each other at 5% LSD level. Soil CEC at different Cr6+ doses 0 µg g$^{-1}$, 100 µg g$^{-1}$, 200 µg g$^{-1}$ and 300 µg g$^{-1}$ did not differ significantly from each other at 5% LSD level. The CEC of rice stubble and modified rice stubble amended soil samples at different incubation period is recorded in Fig. 7. The soil CEC of 30 incubation days increased from the 0 days except Cr100RSB (4.70 Cmolc kg$^{-1}$). In the 2nd sampling CEC of incubated soils decreased significantly. The soil CEC of 90 incubation days increased.

Increase of CEC in 30 and 90 incubation days may be due to pH increase and biochar application. Biochar has higher CEC than soil as a result it increases soil CEC when amended (Fig. 7). On the other hand, modified rice stubble biochar (33.33 Cmolc kg$^{-1}$) increases CEC more than unmodified rice stubble biochar (23.33 Cmolc kg$^{-1}$) due to higher CEC content. The effect of biochar treatments and incubation day on soil CEC is significant at 5% probability level but the applied dose of Cr did not show any effect on soil CEC. The LSD at 5% level showed that soil CEC under RSB and RSB-M treatments differed significantly from each other and control except RSB from control. Soil CEC at different incubation days did not differ significantly from each other but soil CEC content of 0 day from 30 days and 30 days from 60 days differed significantly at 5% LSD level. Soil CEC at different Cr6+ doses 0 µg g$^{-1}$, 100 µg g$^{-1}$, 200 µg g$^{-1}$ and 300 µg g$^{-1}$ did not differ significantly from each other at 5% LSD level.

### *3.2.4. Effects on soil EC*

All incubated soils of 60 days showed decrease of EC result, but EC of soils started to increase during 90 incubation days (Fig. 8). Addition of biochar and modified biochar increases EC by addition of anions and cations in soil. Modified saw dust biochar increases EC more than unmodified saw dust biochar. Both biochar treatments and Cr dose significantly affected EC of the soil ($P$<0.05) while incubation days of submergence did not. LSD at 5% level showed that soil EC under SDB and SDB-M treatments differed significantly from each other and control except SDB from control.

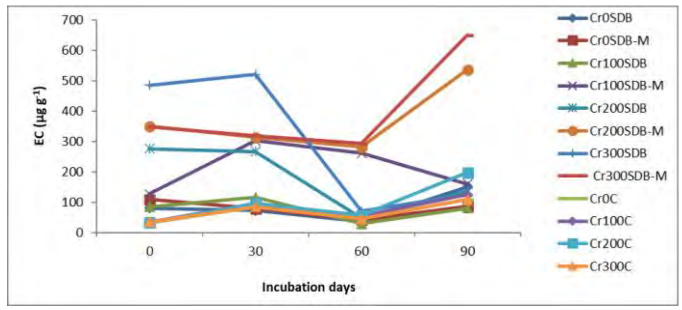


**Fig. 8:** Effect of sawdust biochar and modified sawdust biochar application on soil EC.

Soil EC at different incubation days did not differ significantly from each other at 5% LSD level. Soil EC at 0 µg g$^{-1}$ differed from doses 100 µg g$^{-1}$, 200 µg g$^{-1}$ and 300 µg g$^{-1}$ differed from 100 µg g$^{-1}$ significantly from each other at 5% LSD level. The electrical conductivity of rice stubble and modified rice stubble amended soil samples at different incubation periods (Fig. 9). Rice stubble and modified rice stubble biochar incubated responded differently. There was a gradual decrease of EC of incubated soils during 30 and 60 incubation days. But electrical conductance of soil started increasing during 90 days of incubation (Fig. 9).

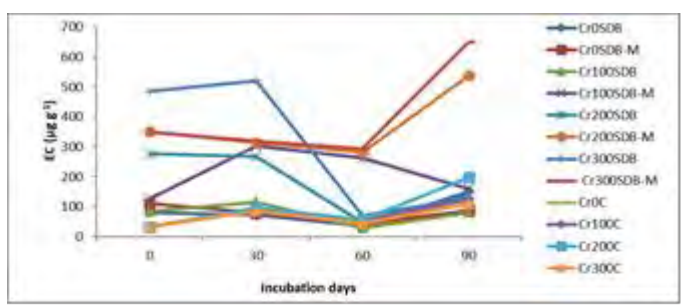


**Fig. 9:** Effect of rice stubble biochar & modified rice stubble biochar application on soil EC.

Cation content of soil changes substantially with addition of biochar and modified biochar of rice stubble. Electrical conductivity of soil during 30 and 60 incubation days samples decreased but incubated soil samples of 90 days showed increase in EC. Since biochar has organic matter and nutrients, its addition increased soil pH, electric conductivity [45]. Normally the addition of biochar and modified biochar increases EC content of soil. But this decrease of EC is probably due to submergence, pH change, and ion concentration of incubated soils. Biochar treatments significantly changed CEC content of the soil at 5% level, but incubation days and Cr dose did not.

### *3.2.5. Effects on soil available N*

In terms of soil moisture content, nitrogen availability changes differently. The availability of nitrogen increased during 30 days of incubation but started decreasing from 60 days and continued till 90 incubation days (Fig. 10). Nitrogen dynamics in soil is a very complex and heterogeneous system. Literatures showed varying results of biochar addition. Biochar sometimes accelerated N dynamics [46] or even sometimes reduced organic N turnover [47]. It is believed that addition of biochar has positive impact on the soil nitrogen dynamics mainly by reducing the leaching loss of nitrogenous compounds [48].

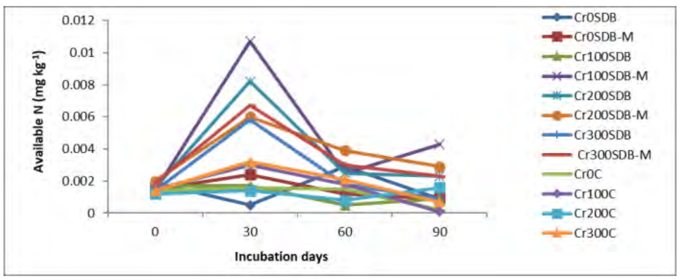


**Fig. 10:** Effect of sawdust biochar and modified sawdust biochar application on soil available N (mg kg$^{-1}$).

Soil initially had the available nitrogen concentration of 0.0014 mg kg$^{-1}$. During 0 to 30 incubation days available N increased from background N level except Cr0SDB, Cr0SDB-M and Cr100SDB treated soil. Soil treated with Cr200SDB shows the highest available N (0.0082 mg kg$^{-1}$). After 60 days of incubation all treatments proved reduced N availability (Fig. 10). Biochar is a high C-to-N ratio material in general; it forms relatively labile and low molecular weight organic compounds; and it may supply a suitable habitat for microorganisms due to its porous structure [49].

The application of biochar improves soil fertility through two mechanisms: either adding nutrients to the soil (such as K, to a limited extent P, and many micronutrients) or keeping nutrients from other sources even from the soil itself and releases it slowly to soil. These characteristics of biochar are suitable for supporting microbial growth and activity and may induce N immobilization in soil as the microorganisms use C from the volatile or labile components within biochar. Biochar might also tighten the soil N cycling through a range of other mechanisms like (i) direct sorption of $NO_{3^-}$, $NH_{4^+}$ organic N species and enzymes on biochar surfaces and pores [47], and (ii) biochar induced organo-mineral associations [50]. Incubation days of submergence and biochar treatments significantly (P<0.05) altered available N content, but Cr doses did not. LSD at 5% level showed that soil available N under SDB and SDB-M treatments did not differ significantly from each other and control except SDB-M from control. Soil available N at 30 incubation days is significantly different from others and control. But available N under different Cr6+ did not differ significantly at 5% LSD level. There is a sharp increase of N availability during 30 days of incubation and a following gradual decrease from 60 to 90 days of incubation (Fig.11).

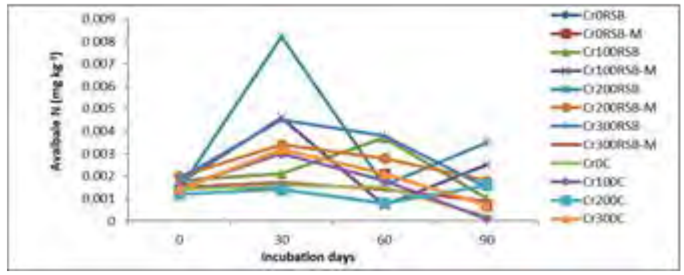


**Fig. 11**: Effect of rice stubble biochar and modified rice stubble biochar application on soil available N (mg kg$^{-1}$).

During incubation available N increased after 30 days except soil treated with Cr0RSB. From 60 days to 90 days available soil N decreased except Cr 100 RSB treatment in 60 days and Cr0RSB, Cr100RSB-M, Cr200RSB treatments in 90 days of incubation. However, it is reported [51] that the sorption capacity of biochar leads to $NH_{4+}$ absorption and, thus, a reduction of the accessibility of $NH_{4+}$ for autotrophic conversion to NO3- and to some extent, biochar was also able to decrease mineral nitrogen ($NH_{4+}$, $NO_3$-). In submerged soils, the main transformations are the accumulation of ammonia, de-nitrification, and nitrogen fixation. These transformations have an important bearing on the nutrition of rice and aquatic plants [51]. Biochar treatments and Cr doses did not have any significant impact on available N content of soil. Only days of submergence put a significant ($P$<0.05) impact on soil N. LSD at 5% level showed that soil available N under RSB and RSB-M treatments did not differ significantly from each other and control except RSB from control. Soil available N at 30 incubation days is significantly different from others and control. But available N under different Cr6+ did not differ significantly at 5% LSD level. As a whole biochar's and modified biochar's contribution to altering soil available N content need to study extensively. Both long- and short-term implication of biochar on N immobilization and mineralization are specific to individual combinations of soil-biochar and further systematic studies are needed to predict agronomic and N cycling responses [52].

### *3.2.6. Effects on soil available P*

There was considerable variation in incubated soil depending on biochar type in P availability. After 30 days of incubation available P content increased from the background level (2.27 mg kg$^{-1}$) except for treatment Cr300 SDB and Cr300SDB-M. Treatment Cr100SDB showed the highest increase (4.70 mg kg$^{-1}$). In 60 days of sampling, the availability of P decreased for the treatments except for Cr0SDB (Fig. 12). In 90 days, sample availability of P decreased. Even the values were less than background level. This may be due to the formation of phosphorus complexes. Phosphorus availability is pH dependent and at near neutral pH, P availability increases [53]. It is possible that the positive exchange sites compete with Al and Fe oxides (e.g., Gibbsite and Goethite respectively) for sorption of soluble P, like that seen for humic and fulvic acids [54]. Days of incubation significantly ($P<0.05$) changed available P of soil, but biochar treatments and Cr doses did not cause any significant alteration of available p content of soil. LSD at 5% level showed that soil available P under SDB and SDB-M treatments did not differ significantly from each other and control.

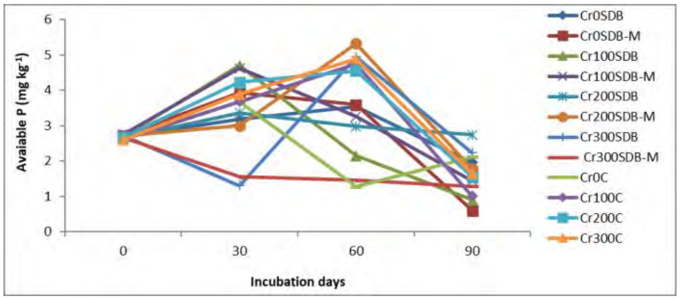


**Fig. 12:** Effect of sawdust biochar and modified sawdust biochar application on soil available P (mg kg$^{-1}$).

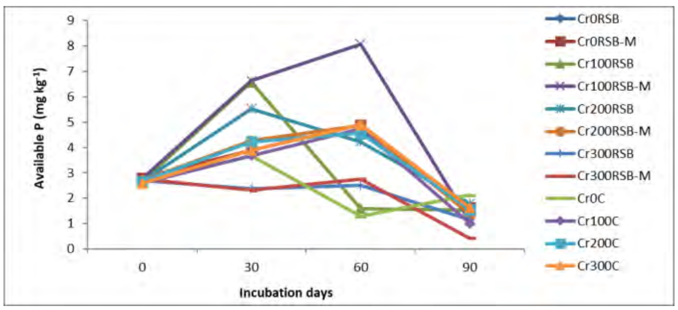


**Fig. 13:** Effect of rice stubble biochar and modified rice stubble biochar application on soil available P (mg kg$^{-1}$).

Soil available P at 30 incubation days differed significantly from each other except 30 days from 0 day and 60 days. But available P under different Cr6+ did not differ significantly at 5% LSD level. Phosphorus availability changes depending on soil pH and biochar types. During 30 days of incubation P availability increased except Cr300RSB and Cr300RSB-M but their value was above background level (2.27 mg kg-1). There was a continuation in the increase of available P after 60 incubation days except for a few but after 90 days P level decreased rapidly (Fig. 13), it might be due to pH of the experimental soil.

Biochar treatments and Cr doses had insignificant impact on soil available P. But incubation days showed a significant impact on soil available P at 5% probability level. LSD at 5% level showed that soil available P under RSB and RSB-M treatments did not differ significantly from each other and control. Soil available P at 30 incubation days differed significantly from each other except 30 days from 60 days reading. But available P under different Cr6+ did not differ significantly at 5% LSD level. From broader study on P availability in ferralsol and ferrosol [55-56], it can be said that biochar application on acidic soils response better for the bioavailability of phosphorus.

### *3.2.7. Effects on soil available K*

Potassium availability varied differently with incubation days. Availability increased at 30 days of incubation but acted differently after 60 and 90 incubation days. Potassium is an essential nutrient for the plants and the function of K is associated with increase of root growth and tolerance to drought, cellulose formation, enzyme activity, support turgor, photosynthesis, increase protein content of plants, protect plants against diseases and nematodes and to reduce water loss [57]. Soil treated with saw dust and modified saw dust showed considerable variation. Modified saw dust amended soil had largest K throughout all incubation days.

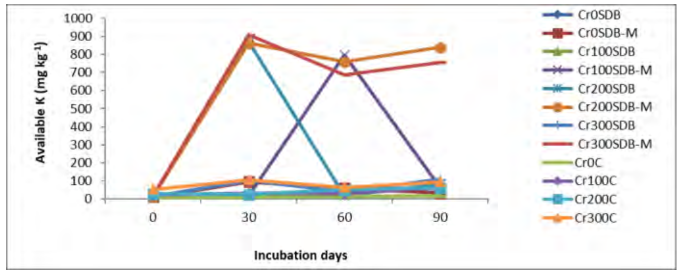


**Fig. 14:** Effect of sawdust biochar and modified sawdust biochar application on soil available K (mg kg$^{-1}$).

At 30 incubation days Cr300SDB-M had highest K (833.27 mg kg$^{-1}$). During 60 and 90 days of incubation Cr100SDB-M and Cr300SDB-M treated soil had highest available K (796.3 mg kg$^{-1}$) and 838.9 mg kg$^{-1}$; Fig. 14). Biochar treatments have a significant impact on available K content of at 5% probability level. But impact of incubation days and doses of chromium in soil available K content were insignificant. LSD at 5% level showed that soil available K under SDB and SDB-M treatments differed significantly from each other and control except SDB from control. Soil available K at 30 incubation days differed significantly from each other except 30 days from 0 day. But available K under different Cr6+ did not differ significantly at 5% LSD level.

Potassium availability of rice stubble and modified rice stubble acted differently. Potassium content increased in 30 and 90 days incubated soils but decreased in 60 incubated soils. However, biochar amended soils showed better K availability than raw soil's background level (6.7 mg kg$^{-1}$). At 30 and 90 incubation days Cr300RSB-M showed highest potassium contents (833.27 and 856.48 mg kg$^{-1}$) and 60 incubation days Cr200RSB-M (796.57 mg kg$^{-1}$). Biochar's with considerable high K content can replace the need for chemical fertilizers. Most K added to the soil will be fixed in the spaces between clay lattice and plants can consume only 1-2% [57]. Due to feverish temperature and rainfall organic fertilizers decompose rapidly.

In contrast, biochar is more stable. The addition of biochar can be a solution to soil with lower potassium. Only biochar treatments altered available K in a significant ($P<0.05$) way while incubation days and Cr doses did not. LSD at 5% level showed that soil available K under RSB and RSB-M treatments did not differ significantly from each other and control except RSB from control.

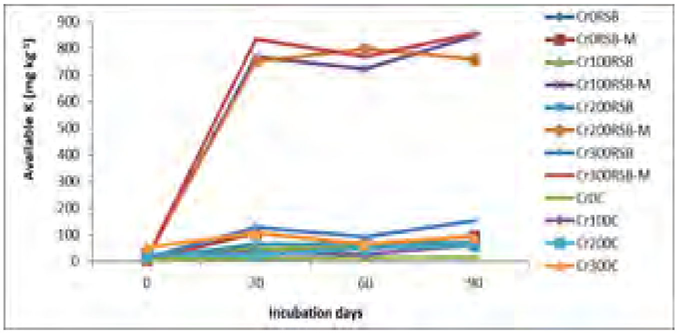


**Fig. 15:** Effect of rice stubble biochar and modified rice stubble biochar application on soil available K (mg kg$^{-1}$).

Soil available K at 30 incubation days differed significantly from each other except 90 days from 0 day (Fig. 15) but available K under different Cr6+ did not differ significantly at 5% LSD level.

### *3.2.8. Effects on soil available S*

Biochar's effect on sulfur varied with various incubation days. Soil incubated with saw dust and modified saw dust biochar showed different results. Availability of sulfur decreased during 30 days of incubation except Cr100SDB-M and Cr200SDB-M. Incubated soils of 60 and 90 incubation days acted diversely. Decrease of sulfur may be due to decrease of mineralization of sulfur under anaerobic submerged condition (Fig. 16). However, soil temperature and moisture regime largely figure out when and how much of organic S is made available to the crop. Biochar addition in mineral soils may also cause sorption of S and ultimately reduce the sulfur availability [58]. There is no significant impact of all the 3 factors on the available S content of soil. LSD at 5% level showed that soil available S under SDB and SDB-M treatments did not differ significantly from each other and control. Soil available S at different incubation days did not differ except 60 days from 0 day and 30 days. Available S under different Cr6+ did not differ significantly at 5% LSD level.

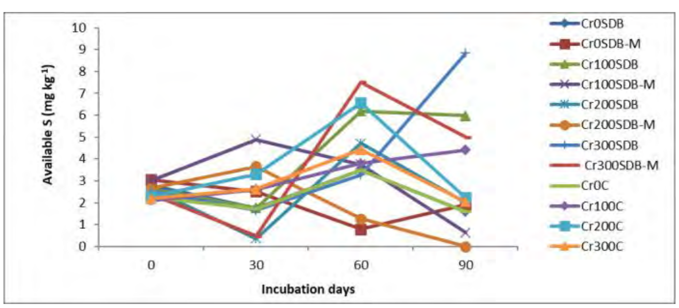


**Fig. 16:** Effect of sawdust biochar and modified sawdust biochar application on soil available S (mg kg$^{-1}$).

Availability of sulfur increased for some incubated soil in both 30 and 60 incubation days decreased for some (Fig. 17). But after 90 days incubation days sulfur content of soils decreased significantly except Cr200RSB.

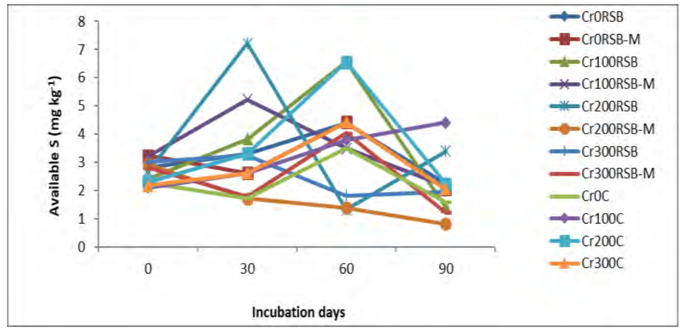


**Fig.17:** Effect of rice stubble biochar and modified rice stubble biochar application on soil available S (mg kg$^{-1}$).

Incubation days of submergence had significant impact and other two factors did not put any significant impact on soil available S content. The LSD at 5% level showed that soil available S under RSB and RSB-M treatments did not differ significantly from each other and control. Soil available S at 60 incubation days differed significantly from 90 days and 0 day and 90 days from 30 days at 5% LSD level but available S under different Cr6+ did not differ significantly at 5% LSD level. Sulfur enriched biochar could be a solution to the problem of sulfur decrease with increasing incubation days.

TABLE 4

PEARSON CORRELATION MATRIX (2-TAILED) FOR PARAMETERS OF INCUBATED SOILS AFTER APPLICATION OF UNMODIFIED AND MODIFIED BIOCHAR OF SAW DUST.

| | pH | EC | CEC | Avail.N | Avail.P | Avail.S | Avail.K | OC | Cr(VI) |
|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | -.145 | -.150 | .133 | .189 | .124 | .034 | -.195 | -.088 |
| EC | -.145 | 1 | .312* | .452** | -.252 | -.111 | .607** | -.002 | .064 |
| CEC | -.150 | .312* | 1 | .163 | -.091 | -.072 | .397** | -.123 | -.211 |
| Avail.N | .133 | .452** | .163 | 1 | .176 | -.158 | .490** | -.159 | -.099 |
| Avail.P | .189 | -.252 | -.091 | .176 | 1 | -.008 | -.081 | .090 | .111 |
| Avail.S | .124 | -.111 | -.072 | -.158 | -.008 | 1 | -.084 | -.033 | -.002 |
| Avail.K | .034 | .607** | .397** | .490** | -.081 | -.084 | 1 | -.42** | -.264 |
| OC | -.195 | -.002 | -.123 | -.159 | .090 | -.033 | -.415** | 1 | .261 |
| C(VI) | -.088 | .064 | -.211 | -.099 | .111 | -.002 | -.264 | .261 | 1 |

*, ** significant at P<0.05 and P<0.01, respectively.

TABLE 5

PEARSON CORRELATION MATRIX (2-TAILED) FOR PARAMETERS OF INCUBATED SOILS AFTER APPLICATION OF UNMODIFIED AND MODIFIED BIOCHAR OF RICE STUBBLE.

| | pH | OC | EC | CEC | Avail.N | Avail.P | Avail.K | Avail.S | Cr(VI) |
|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | -.349* | .052 | .069 | .316* | .206 | .063 | .130 | .064 |
| OC | -.39* | 1 | .094 | -.195 | -.015 | -.024 | -.317* | -.159 | .169 |
| EC | .052 | .094 | 1 | .515** | .128 | -.126 | .537** | -.150 | .023 |
| CEC | .069 | -.195 | .515** | 1 | .282 | .169 | .643** | -.060 | -.157 |
| Avail.N | .316* | -.015 | .128 | .282 | 1 | .284 | .095 | .349* | .076 |
| Avail.P | .206 | -.024 | -.126 | .169 | .284 | 1 | .083 | .423** | -.080 |
| Avail.K | .063 | -.317* | .537** | .643** | .095 | .083 | 1 | -.204 | -.371** |
| Avail.S | .130 | -.159 | -.150 | -.060 | .349* | .423** | -.204 | 1 | -.032 |
| Cr(VI) | .064 | .169 | .023 | -.157 | .076 | -.080 | -.371** | -.032 | 1 |

*, ** significant at P<0.05 and P<0.01, respectively.

The high dependencies between parameters of incubated soils after application of modified and unmodified biochar of saw dust and rice stubble showed are confirmed (Table 4 and Table 5). At the same time, variability of correlations is seen even in the case of soil parameters found near each other. This reflects the role of individual soil parameters of both modified and unmodified biochar's application of saw dust and rice stubble. Furthermore, correlation between incubated soils parameters after application of modified and unmodified biochar of saw dust and rice stubble are strongly significant to enhance soil fertility and more tolerable Cr polluted soils.

## IV. CONCLUSIONS

The present study aims at preparing biochars from agricultural residues like rice stubble and saw dust, modifying them with strong alkali KOH, and assessing their impact on nutrient status of Cr contaminated soil. In this experiment, the characteristics of different biochars analyzed vary significantly depending on the type of feedstocks and modification. Variations are seen in their surface properties, physicochemical properties, and nutrient contents. The results obtained in this study revealed that addition of biochar increased soil pH, EC, CEC, available P, K, N and significantly reduced Cr(VI) of chromium polluted soils. The highest chromium reduction was seen where modified biochars were applied. Therefore, it has very strong evidence application of both biochar and modified biochar been imperative to increase soil fertility, enhance nutrient uptake, improve Cr polluted soils, and can play a vital role in developing a sustainable system of agriculture.

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