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AQUEOUS REMOVAL OF CARBOFURAN AND 2,4-D USING SUSTAINABLE BIOCHARS DEVELOPED FROM AGRICULTURAL BYPRODUCTS.

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Abstract

Contamination of surface and sub-surface water; and piling up of waste are among major environmental concerns nowadays. A sustainable approach devising the utilization of a potential waste to do way with other pollutant is the need of the hour. In the current study, biochar obtained from the agricultural byproducts i.e. rice husk, corn stover, corn cob and sorghum stem were used for aqueous remediation of carbofuran and 2,4-D. Remediation process employed here is called adsorption which is a surface phenomenon involving multi-component fluids (gas/liquid) attracted to the surface of a solid adsorbent. Here, rice husk biochar (RHBC), corn stover biochar (CSBC) cob biochar (CCBC) and sorghum stem biochar were developed from respective feedstock at 900°C. Batch experiments were carried out at different pHs i.e. 2-10. Maximum carbofuran removal of 86.35% was obtained by CSBC occurred at pH 4.0 (at an adsorbent dose of 5 g/L and carbofuran concentration of 5 mg/l at 25°C). Similarly, maximum 2,4-D removal of 72.52% was obtained by CCBC at pH 6 (at an adsorbent dose of 5 g/L and carbofuran concentration of 5 mg/l at 25°C).

Key words: *Carbofuran, 2,4-D, Biochar, Adsorption, rice husk, corn stover, corn cob, sorghum*

INTRODUCTION

Use of pesticides for agriculture, forestry and other associated activities has increased massively nowadays (Grube et al., 2011). These pesticides often reach different surface and subsurface water bodies through spray drift, runoff, and subsurface flow leading to their contamination (Zhang et al., 2018). Considered as priority pollutant (Keith and Telliard, 1979), pesticides exhibit high toxicity, persistance bioaccumulation tendencies and carcinogenicity (Damlas and Eleftherohorinos, 2011). Different pesticides are reported in surface as well as ground water in India and world (Stehle and Schulz, 2015). Insecticides and herbicides constitute major categories of pesticides used in world (Qurratu and Reehan, 2016).

Carbofuran, an insecticide and 2,4-D, a herbicide are among most widely used pesticides (Gupta et al., 2006). The guideline values for carbofuran and 2,4-D in drinking water, based on allocation to water, weight of individual and consumption is 0.007 and 0.03 mg/L, respectively (WHO, 2017). Various methods of water treatment for removal of pesticides include photocatalytic degradation (Gong et al., 2011), electrochemical degradation (Miwa et al., 2006), ultrasound combined with photo-Fenton (Katsumata et al., 2011), advanced oxidation processes (Zhou et al., 2011), aerobic degradation (Murthy and Manonmani, 2007), electrodialysis membranes (Banasiak et al., 2011), nanofiltration (Ahmed et al., 2008), ozonation (Maldonado et al., 2006), biosorption (Deng et al., 2009) and adsorption (Danish et al., 2010). Advantages and drawbacks of these methods have been extensively discussed by different research groups (Foo and Hameed, 2010). Among these methods, adsorption has emerged as a promising technique due to its versatility, simplicity and low operation cost. High removal capacity and wide applicability of adsorption technique also make it efficient for pesticide removal (Salman, 2013). Adsorption is a surface phenomenon where an adsorbate (solute from a solution) gets accumulated over an adsorbent (solid porous material) due to liquid-solid intermolecular forces of attraction (Rashed, 2013). A variety of adsorbents such as agricultural wastes, bioadsorbents, polymeric compounds, industrial wastes, inorganic wastes, and carbonaceous adsorbent are used for pesticide removal from aqueous medium either in their simpler or modified form (Ahmad et al., 2010). Carbonaceous adsorbents are majorly constituted by activated carbons (ACs), carbon nanoparticles and biochars developed from different feedstocks (Shan et al., 2015). But preparation of activated carbon and nanoparticles is very costly which paves way for a renewable, low cost and rather sustainable option- biochar (Mohan et al., 2014). Biochar is very stable, recalcitrant and carbon-rich in nature and is obtained by carbonization of biomass (Ahmad et al., 2014). Apart from pyrolysis condition such as temperature, heating rate and resideance time biochar properties are also affected by nature of feedstock (Kloss et al., 2012). Agro-forestry residues along with milling residues, municipal waste and animal manures are used as feedstock for biochar development (Lehmann et al., 2006). Rice (*Oryza sativa*), maize (*Zea mays*) and sorghum (*Sorghum bicolor*) are among most valued food crops of India. Importance of these three crops can be understood both in terms of area under cultivation for these crops as well their production. Average yearly production of 108.5 million tons (in 431.3 lac hectares), 25.27 million tons (in 89.70 lac hectares) and 4.51 million tons (in 53.7 lac hectares) was reported for rice, maize and sorghum respectively during years-2015-2018 (DACFW, 2018). Along with the crop yield, the byproducts or residue produced i.e. husk, straw, stover, cob, and stalks of these crops are also of great significance (Daioglou et al., 2016). Estimates of by-products produced from these crops can be assessed using residue to production ratio (RPR) values. RPR is the gravimetric ratio of residue (by-products) to the actual crop yield (Murli et al., 2008). On the basis of production of respective crops and individual RPR value of by-products i.e. rice straw (1.5), rice husk (0.2), corn stalk (2), corn cob (0.33), sorghum cob (0.5), sorghum husk (0.2), and sorghum stalk (1.7) the total by-product generated can be quantified (Hiloidhari et al., 2014). So, development of biochar from these agricultural byproducts will serve dual purpose of agro-waste management as well as pesticide remediation from water.

2. MATERIAL AND METHODS

2.1 Preparation of stock solution.

Stock solutions (100 mg/L) of carbofuran and 2,4-D were prepared by dissolving 100 mg of carbofuran and 2,4-D, respectively in 1000 ml of double distilled water in a volumetric flask. The working solutions of 5 mg/L was prepared by using this stock solution. The pHs of the working solutions were maintained by using HCl (0.1N) and NaOH (0.1N).

2.2. Development of biochar

Agricultural byproducts viz. rice husk, corn stover, corn cob and sorghum stem were collected from Bhikhanpur village, Gaziabad, Uttar Pradesh, India. They were sun-dried for 2 weeks. Post drying they were cut in small size of 1-2 cm and pyrolysed separately in quartz crucibles in muffle furnace (Thermo-scientific) at 900°C (ramp rate-10°C/min and residence time of 30 minute) to form biochar. Obtained biochars i.e. RHBC, CSBC, CCBC and SSBC were crushed, sieved, washed and filtered with double distilled water to remove any possible color leach. After washing CCBC was oven dried and sieved again with 30-50 BSS mesh size sieves to ensure uniform particle size. The scheme for development of biochars is mentioned in figure 1.

2.3 Sorption process

Sorption studies were carried out at different pH to assess its impact on carbofuran and 2,4-D removal by the RHBC, CSBC, CCBC and SSBC

2.3.1 Effect of pH

This study determines the optimum pH for the sorption process. For this study, 0.25 g RHBC, CSBC, CCBC and SSBC taken in separate plastic beakers. 50 mL of working solution having initial carbofuran concentrations of 5 mg/L at pH range of 2-10 were added to them. Similar task were performed with the biochars and working solution of 2,4-D with initial concentration 5 mg/L (pH range- 2-10). Now, the suspension of biochars and pesticides were agitated in water bath shaker (80-120 rpm) for 24 hours at 25 ^{0}C. Thereafter, solutions were filtered using syringe filters of pore size, 0.2 µm. The filtrates were analyzed on UV/Vis spectrometer Lambda 35, Perkin Elmer. The absorption maxima (λ_{max}) for carbofuran and 2,4-D were 275 and 284 nm, respectively. Carbofuran and 2,4-D concentration in the samples were determined from equation y=mx +C from plots of absorbance versus specific concentration of their standard solution.

The percentage 2,4-D removal and adsorption capacity were determined using equation 1 and 2, respectively.

$$\text{Removal efficiency (\%)} = \frac{(C_o - C_e)}{C_o} \text{ x } 100 \quad (1)$$

$$\text{Adsorption capacity, } q_e = \frac{(C_o - C_e)}{M} \text{ x } V \quad (2)$$

Where, C_o (mg/L) and C_e (mg/L) are the initial concentration and is the equilibrium concentration of the pesticide solution, respectively. q_e (mg/g) is the amount of pesticide adsorbed per gram of the biochars, V (L) is the volume of the pesticide solution taken, and M (g) is the quantity of the biochar added.

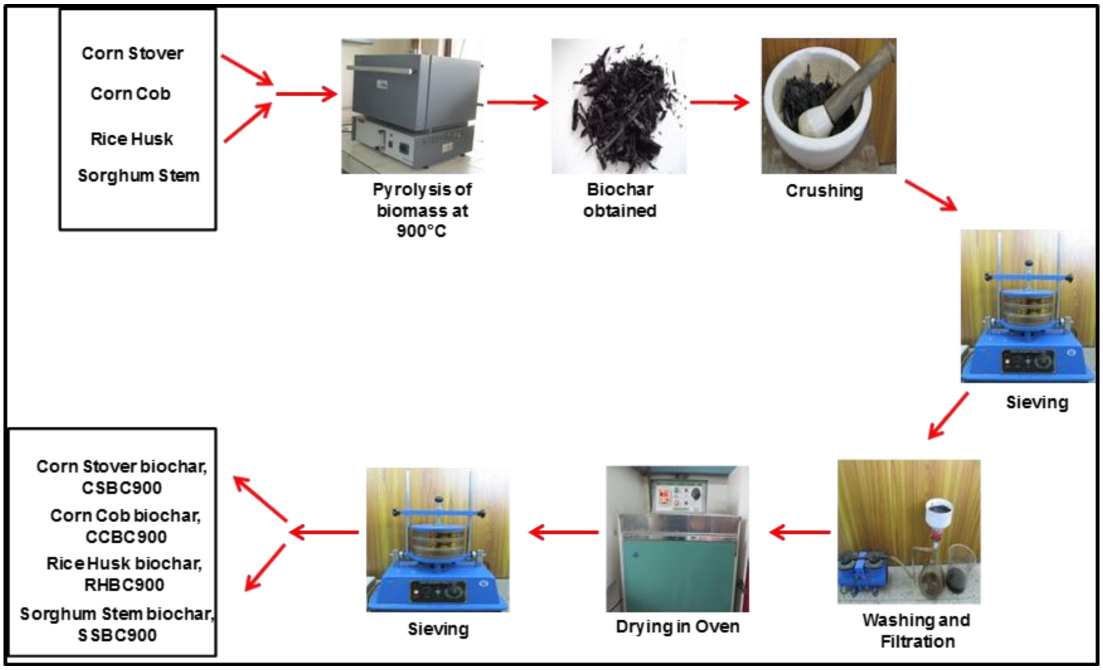

Figure 1. Development of RHBC, CSBC, CCBC and SSBC from agricultural byproducts

3. Results and discussions

Table 1: Carbofuran adsorption capacities of biochars at different pH

	q_e (RHBC) (mg/g)	q_e (CSBC) (mg/g)	q_e (CCBC) (mg/g)	q_e (SSBC) (mg/g)
pH- 2	0.52	0.64	0.61	0.79
pH- 4	0.94	0.98	0.86	0.82
pH- 6	0.92	0.89	0.93	0.92
pH- 8	0.75	0.91	0.83	0.78
pH- 10	0.61	0.70	0.70	0.54

Table 2: 2,4-D adsorption capacities of biochars at different pH

	q_e (RHBC) (mg/g)	q_e (CSBC) (mg/g)	q_e (CCBC) (mg/g)	q_e (SSBC) (mg/g)
pH- 2	0.34	0.55	0.62	0.52
pH- 4	0.50	0.72	0.72	0.54
pH- 6	0.39	0.76	0.81	0.71
pH- 8	0.64	0.72	0.48	0.45
pH- 10	0.52	0.60	0.48	0.62

Apart from the properties of the adsorbent and adsorbate, the adsorbent-adsorbate interaction is greatly affected by the solution pH. This effect is due to change in behavior of adsorbate, and possibly the adsorbent too with change in pH of the solution in which they are present. Though sometimes the change is trivial and can be ignored within the small range but it certainly has to lay an impact when considered across extremes of pH. Here in the case of carbofuran adsorption onto RHBC, CSBC, CCBC and SSBC [Figure 2 (a-d)] the variation in the percent removal across the pH 2 to 10 is not that much. Though unlike other similar studies the carbofuran removal by biochars is least at pH 2 except for SSBC. Percent carbofuran adsorption by RHBC is 61.72, 82.85, 82.93, 70.48 and 67.24% at pH 2, 4, 6, 8 and 10, respectively [figure 2 (a)].

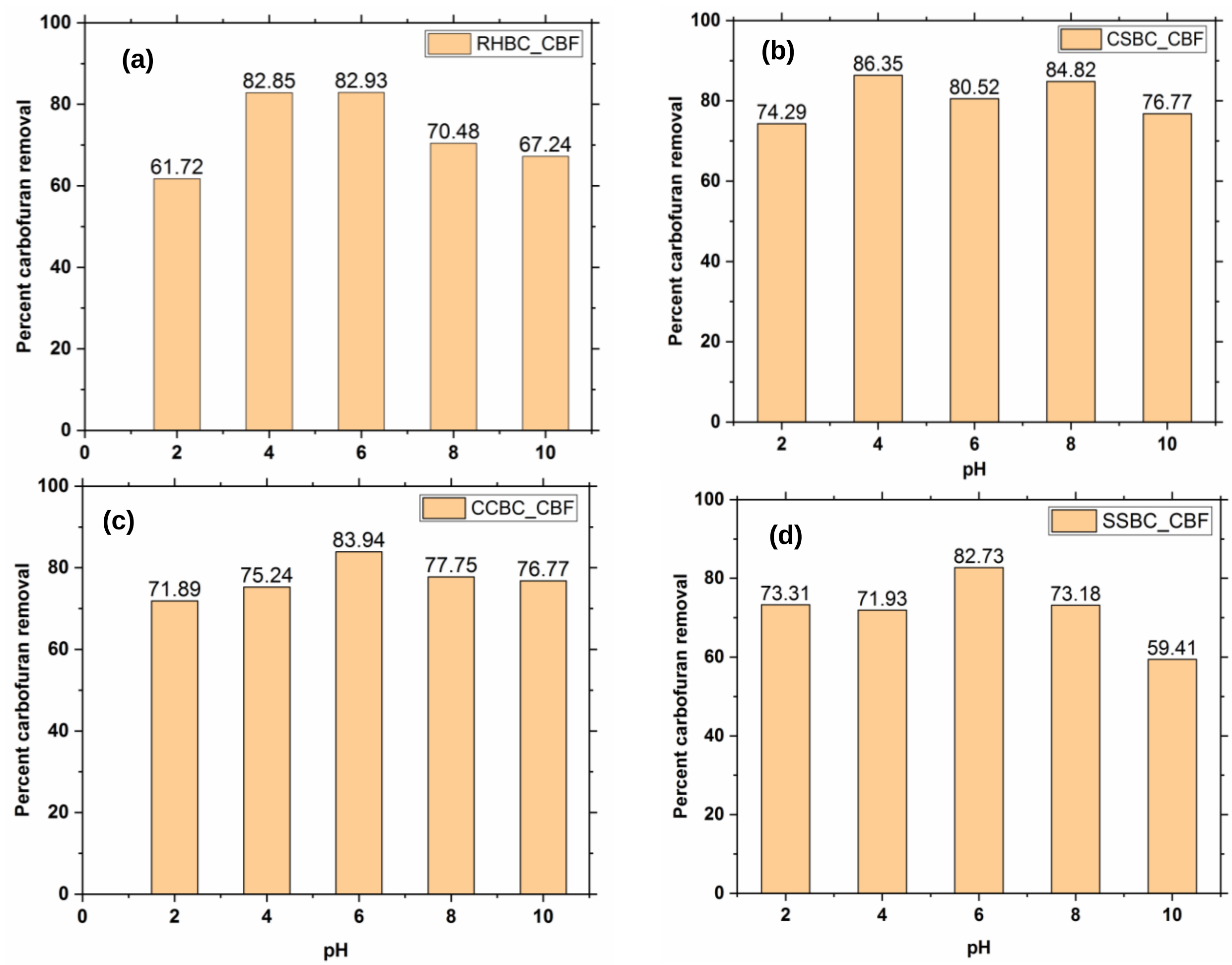

Figure 2: Percent carbofuran removal by (a) RHBC, (b) CSBC, (c) CCBC and (d) SSBC

For CSBC adsorption is 74.29% at pH 2 but it seem to catch up with increase in pH i.e. 86.35, 80.52, and 84.82% at pH 4, 6, and 8, respectively before reducing to 76.77% at pH 10 [Fig 2 (b)]. Carbofuran adsorption onto CCBC displays similar trends of variation in percentage adsorption with change in initial pH [Figure 2 (c)]. Here percent removal is observed to be 71.89 % at pH 2 which increases until 75.24 and 83.94% at pH 4 and 6 respectively. At afterwards pH i.e. 8 and 10 the order of variation is reversed and percent adsorption reduces marginally to 77.75 and 76.77%, respectively. Similarly, percent carbofuran adsorption by SSBC is 73.31, 71.93, 82.73, 73.18 and 59.41% at pH 2, 4, 6, 8 and 10, respectively [Figure 2(d). A variation in equilibrium pH with respect to initial pH is also noted during the experiment. It is observed that the equilibrium pH remains nearly the same for initial pH 2 and 10 but increases considerably in intermediate range of pH i.e. 4, 6 and 8. General trend of percent carbofuran adsorption being affected by pH may be attributed to its pH based speciation (pka value – 3.78) and pHzpc based charged distribution on the surface of biochars (Vimal et al., 2019).

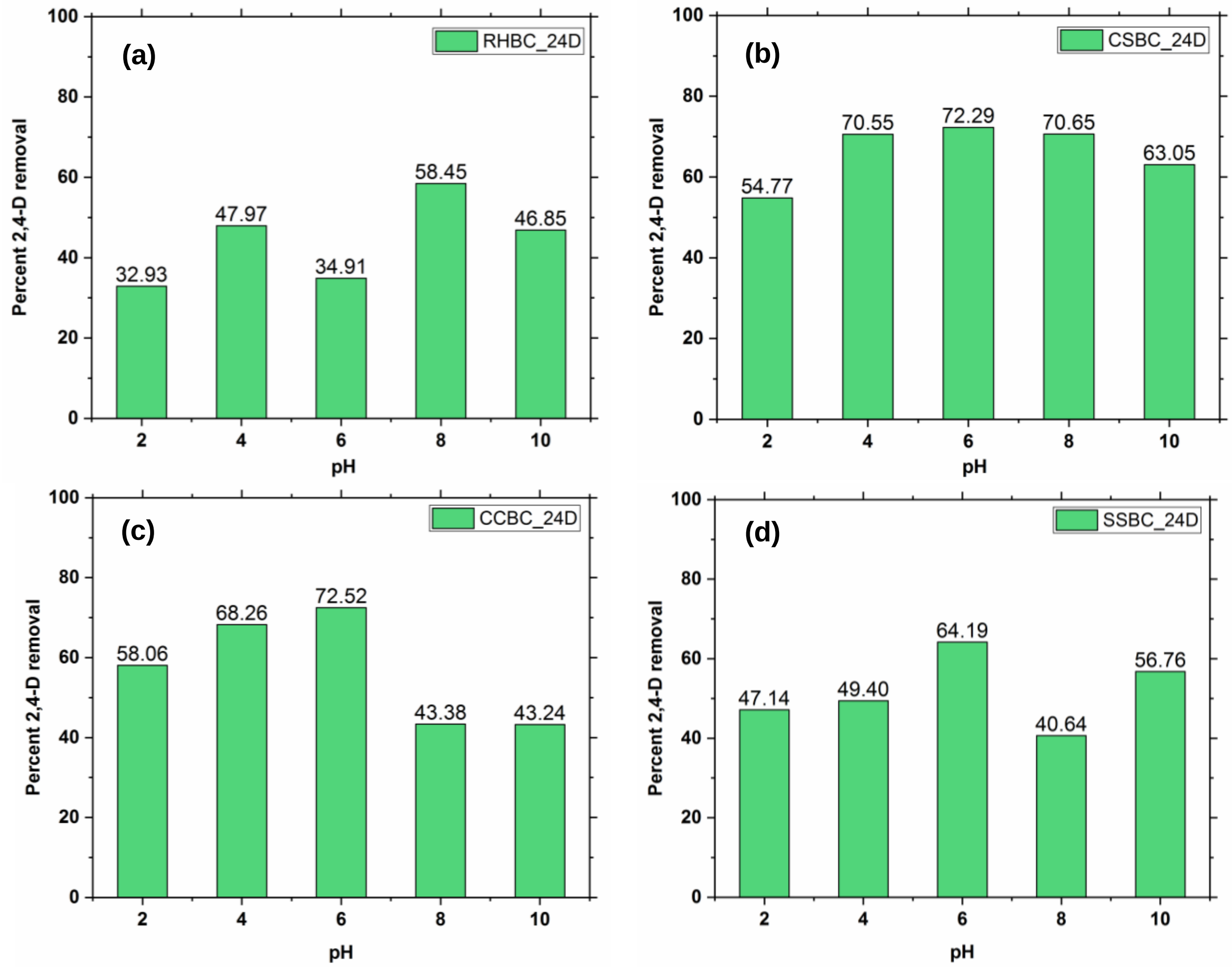

Figure 3: Percent 2,4-D removal by (a) RHBC, (b) CSBC, (c) CCBC and (d) SSBC

Similarly, aqueous removal of 2,4-D is also affected by the solution pH. Here in Figure 3(a-d), we can see that there is variation in percent 2,4-D adsorption by different biochars at different pH. Percent 2,4-D removal is least for RHBC among all biochars at all the pH. For carbofuran adsorption by RHBC, percent removal of 32.93, 47.97, 34.91, 58.45 and 46.85% is obtained at pH 2, 4, 6, 8 and 10, respectively [Figure 3 (a)]. 2,4-D adsorption on CSBC increases initially with increase in solution pH from pH 2 to pH 6 i.e. 54.77 to 72.29%. This increase is significant and in order of more than 15%. It is observed that the removal efficiency reduces afterwards to 70.65 and 63.05 % at pH 8 and 10, respectively [Figure 3 (b)]. Carbofuran follows similar order of increase in percent absorption up to pH 6 but with greater uniformity for CCBC. Percent adsorption of 58.06, 68.26 and 72.52 at pH 2, 4 and 6, respectively. Afterwards this removal efficiency reduces and remains almost same at pH 8 and 10 i.e. 43.38 and 43.24%, respectively [Figure 3 (c)]. At pH 10 too, the reduction in percent 2,4-D removal is quite less and hovers at 60.40%. On the other hand, 2,4-D adsorption onto SSBC is quite similar to CCBC in terms of trends but is lesser in terms of magnitude. As given in figure 3(d), the percent 2,4-D adsorption for SSBC increases from 47.14 to 49.40% and later to 64.19 % with rise in pH of the solution from 2 to 6. Here, variation in 2,4-D removal efficiency is found to be of significant i.e. more than 10%. At pH 8, the removal efficiency takes a bigger dip of more than 10% and falls sharply to 40.64 but increases again to 56.76% at pH10. The change in equilibrium pH have similar trends for all biochars i.e. slight or no increase, increase, and slight decrease for initial pH 2, pH range 4-8 and pH 10, respectively. Here too, variation in percent 2,4-D adsorption with change in pH may be attributed to dissociation of 2,4-D (pka value – 2.81), behavior of phenoxyacetate ion and pHzpc based charged distribution on the surface of biochars (Essandoh et al., 2017). Adsorption capacities (q_e) for the biochars at different for carbofuran and 2,4-D removal at different pH are given in table 1 and table 2, respectively.

CONCLUSIONS

Carbofuran and 2,4-D adsorption are minimum and maximum at pH 2 and pH 6, respectively for all the biochars. Maximum carbofuran removal of 86.35% was obtained by CSBC whereas maximum 2,4-D removal of 72.52% was obtained by CCBC. Adsorption capacities of all the biochars is less than 1 at all the pH. These biochars show best removal efficiency at pH- 6 i.e. pH of water found naturally so they can be used as low cost adsorbent for aqueous carbofuran and 2,4-D remediation in natural conditions.

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