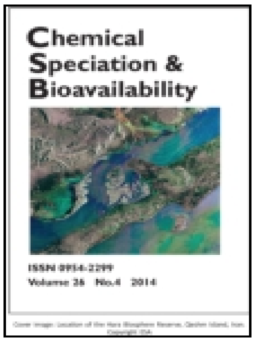

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Interface interactions between insecticide carbofuran and tea waste biochars produced at different pyrolysis temperatures

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ABSTRACT
Biochars showed a potential as adsorbents for organic contaminants, however, have not been tested for carbofuran, which has been detected frequently in water. This study provides evidences for the use of infused tea residue derived biochar for carbofuran removal. Biochars were produced at 300, 500 and 700 °C by slow pyrolysis and were characterized by proximate and ultimate analysis, FT-IR, SEM, BET and pore size distribution. Pyrolysis temperature showed a pronounced effect on biochar properties. The maximum carbofuran removal was achieved at pH 5. Freundlich and Temkin models best fit the equilibrium data. Biochars produced at 700 °C showed the highest sorption intensity. The adsorption process was likely to be a favorable chemisorption process with electrostatic interactions between carbofuran molecules and biochar surface. Acid-base interactions, electrophilic addition reactions and amide bond formations are the possible mechanisms of carbofuran adsorption. Overall, biochars prepared from tea waste can be utilized as effective adsorbents for removal of aqueous carbofuran.

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Isotherm modeling; black carbon; pesticide; chemisorption; slow pyrolysis

1. Introduction

Pesticides are intensively used for preventing, destroying, repelling any pest in agricultural practice. Worldwide use of pesticides has increased dramatically during the last two decades.[1] Presently, >600 different pesticide formulations are being used in our environment. Due to the widespread use of pesticides, their residues are found in the environment. Moreover, the presence of pesticides in the environment has caused great environmental and social concerns.[2] There are several different classes of pesticides including organochlorines, organophosphates, carbamates and pyrethroides. Carbofuran is a broad spectrum systemic pesticide included in the group of carbamate.[3] Though use of carbofuran is banned in Europe and some other countries, it is still widely used in Africa and Asia for the control of soil dwelling and foliar feeding insects in many crop cultivations such as potatoes, corn, rice and grapes. During 2000–2005 period of time, 939–1068 metric tons of carbofuran have been sold in Sri Lanka.[4] Furthermore, carbofuran is known to be more persistent than other carbamate or organophosphate insecticides and it is often detected in portable water.[3]

Carbofuran contamination commonly occurs in many agricultural areas worldwide. In Kenya, carbofuran and its metabolites have been recorded from water samples (0.005–0.495 mg L^{-1}) in the farmlands.[5] Carbofuran was also detected in water samples (0.198 mg L^{-1}) collected from paddy and vegetable fields in Bangladesh.[6] Carbofuran residues were reported in well waters from Punjab, Pakistan at the concentration of 0.023 mg L^{-1}.[7] According to USEPA, maximum permissible limit of carbofuran in drinking water is 0.04 mg L^{-1} whereas the World Health Organization specifies the permissible limit of 0.007 mg L^{-1}. There are considerable risks associated with carbofuran when present in food and drinking water. High oral toxicity of carbofuran was determined to be 11 mg kg^{-1} body weight in rats. Exposure to carbofuran causes negative impacts on human reproductive systems and inhibitory effects on acetyl cholinesterase activity at central cholinergic and at neuromuscular junctions. Moreover carbofuran is quite toxic to fish and bird species and produces mortality in 50% of the population.[8,9] As carbofuran contains 166 µg kg^{-1} amount of arsenic, a group of academia had suggested the usage of carbofuran may be one of the possible contributions for chronic kidney disease of unknown etiology in north central and Uva province in Sri Lanka.[10]

Several methods including ion exchange,[11] precipitation,[12] adsorption [13] and membrane separation

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[14] are reported in literature to remove pesticides from water. Among them, adsorption is one of the most frequently used methods because of its efficiency and applicability for treating carbofuran contaminated waters. Activated carbon is one of the widely used adsorbents for carbofuran removal.[15] Several authors reported the feasibility and effectiveness of activated carbon derived from different feedstocks such as coal, rice straw, banana stalks, date seeds, palm oil fronds for removing aqueous carbofuran.[15,16] However, use of activated carbon is not cost effective for practical application and restricted for small-scale, often remote communities or developing countries. Thus, there is a need to search for its substitute which is cheaper and environmental friendly.

In recent years, the search for low-cost adsorbents with pollutant binding capacities has intensified. Similarly, attempts have been made to develop such types of inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Biochar (BC), the solid material resulted from the biomass pyrolysis under limited or no oxygen, is emerging as an alternative to activated carbon with cost-effective and environmental advantages. Biochar resembles activated carbon in some aspects having a structured carbon matrix and a medium to high surface area indicating that it may act as a surface sorbent. Biochar preparation requires less energy versus activated carbon.[17] Slow/fast pyrolysis or gasification processes could be used for making the BCs from feedstocks as crop residues, animal manures, solid waste etc.[18] However, biomass selection and pyrolysis temperature are crucial factors because they may determine the quality and economic feasibility.[17] Up to now no studies are available on the possible use of BC for carbofuran remediation in aqueous media and hence, a substantial understanding is required to ensure its efficiency to remove such priority pollutants. Besides, understanding the adsorption mechanism is of importance in practical applications. Physical or chemical adsorption mechanism behind is strongly dependent on BC properties (porous structure, ash content, functional groups, polarity, pH etc.) which are influenced by the nature of feedstock and the operating conditions of the manufacturing process.[19] The significance of electrostatic attractions in carbofuran adsorption, which are due to the dissolution of oxygen containing functional groups on adsorbent surface, have been discussed.[15] Moreover equation parameters of equilibrium isotherm models often provide insights into adsorption process and more accurate isotherm descriptions are crucial to predict sorption phenomena. Most studies from the literature have reported that the adsorption of pesticides on carbonaceous materials was well represented by Freundlich model.[16,20] Some researchers have shown that adsorbents prepared from thermal treatments like pyrolysis exhibited a more diverse range of isotherms indicating the heterogeneous nature of adsorption process.[19] Nevertheless, carbofuran adsorption mechanisms on to BCs have not been adequately described yet.

Leaves from *Camellia sinensis* are used to prepare tea products and they are widely used throughout the centuries in Sri Lanka as a popular aromatic beverage. Nevertheless, infused tea residue is discarded to the environment on large scale as a waste material. Therefore, BC production may be useful rather than throwing it directly into the environment. In our earlier study,[21] BCs derived from tea waste was used to depurate pharmaceuticals from contaminated water. Excellent performance of tea waste biochar (TWBC) for pharmaceutical sulfamethazine removal was obtained. This study evaluates the effectiveness of TWBCs produced at different pyrolysis temperatures for carbofuran adsorption aiming towards to see its universal potential on many different pollutants. Here, we report the carbofuran removal capacities for TWBCs for the first time together with BC properties produced at different pyrolysis temperatures.

2. Material and methods

2.1. Biochar and chemicals

Disposed infused tea residues were collected from restaurants in Kandy city of Central Province, Sri Lanka. Tea residues were washed several times with distilled water and dried in an oven at 60 °C for 48 h. The dried feedstock was ground to <1 mm particle size and slow pyrolyzed using a muffle furnance (model P330, Nabertherm, Germany) under limited oxygen. Heating rate (7 °C min^{-1}), pyrolysis time (3 h) and final pyrolysis temperature (300, 500 and 700 °C) was maintained by a control program. Gaseous N_2 was purged at a rate of 5 mL min^{-1} in oder to remove organic or gaseous by-products. After the completion of pyrolysis reaction, BC samples were allowed to cool overnight and designated as TWBC300, TWBC500 and TWBC700. The yield of BCs was determined by proportion of biochar to biomass. Technical grade carbofuran (99.9%) was purchased from Sigma-Aldrich, USA. All other chemicals used in this study were analytical grade from Fluka (Switzerland) or Sigma-Aldrich. Distilled deionized water (resistivity: 18.2 MΩcm^{-1}) was used to prepare all the solutions.

2.2. Biochar characterization

The pH and EC of BCs were measured in deionized water at 1:10 w/w ratio using a digital pH meter (model 702SM, Metrohm, Switzerland) and electrical conductivity meter (model 5 STAR, Thermo Scientific, Environmental Instruments, USA), respectively. Proximate analysis was carried out according to the ASTM D1762–84 Standard Method.[22] The moisture content of BCs was determined by drying the samples at 105 °C for overnight. The volatile matter content was estimated by heating the BCs in covered crucibles at 450 °C for 1 h. Ash content was measured by heating samples in an open top crucible at 750 °C for 1 h. Finally, the weight percentage of fixed carbon was calculated from ash, volatile matter and moisture contents. The elemental composition (C, H, N, S and O) was determined using dry combustion method (model Vario MAX CN, elementar, Hanau, Germany). Molar H/C and O/C ratios were also calculated as indicators of aromaticity and polarity respectively. Alkaline metals including Na, K, Ca and Mg amounts were determined using ICP-OES (Perkin Elmer OES optima 4300DV).

FTIR spectra were obtained in the range of 400–4000 cm^{-1} by a Nicolet FTIR spectrophotometer (model 6700, USA) using sample pellets prepared with fused KBr. Surface morphology of BCs was examined by field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive spectrophotometer (model SU8000, Hitachi, Tokyo, Japan). Surface area, pore volume and pore diameters of BCs were already determined in our earlier study [21], using standard procedures.

2.3. Batch sorption experiments

Carbofuran stock solution (1000 mg L^{-1}) was prepared with deionized water. A series of adsorbate solutions ranging from 5 to 100 mg L^{-1} were prepared and buffered at pH 5.0 with acetate buffer. Adsorption experiments were conducted at pH 3, 5, 7 and 9 on the basis of the pH range typically found in the water and wastewater. The buffers of pH 3–5 were prepared by mixing appropriate volume of sodium acetate (0.1 M CH_3COONa) and acetic acid (0.1 M CH_3COOH). Buffer solutions of pH 7–9 were prepared by mixing aqueous ammonia and phosphoric acid with ammonium phosphate solution (0.1 M $(NH_4)_3PO_4$). A dose of 1.5 g L^{-1} BC was added into the solutions and samples were equilibrated in a mechanical shaker (model EYELA B603) at room temperature (30 °C) for 4 h at 100 rpm. After equilibration, each sample was filtered using a Millipore membrane filter (0.45 µm). The filtrate was analyzed for carbofuran at 276 nm using a double beam UV–Vis spectrophotometer (model UV-160A, Shimadzu, Japan) and remaining carbofuran concentrations were obtained from the calibration curve plotted by using 6 appropriate standards 5, 10, 20, 50, 75, 100 mg L^{-1}.

3. Calculations

The amount of carbofuran adsorbed onto the BCs was calculated using Equation 1 [23,24]:

$$q_e = \left[C_0 - C_e\right] V M^{-1} \tag{1}$$

where q_e is the carbofuran amount adsorbed on BCs (mg g^{-1}); C_0 and C_e are the initial and equilibrium carbofuran aqueous phase concentrations (mg L^{-1}); V is the solution volume (L) and M is the biochar mass (g). The Freundlich (Equation 2), the Langmuir (Equation 3), the Temkin (Equation 5), the Dubinin-Radushkevich (Equation 6) and the Redlich–Peterson (Equation 8) adsorption isotherm models were employed to fit the carbofuran adsorption data using Origin 6.0 software.

$$q_{ads} = K_F C_e^n \tag{2}$$

$$q_{ads} = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

where, q_{ads} is the amount of carbofuran adsorbed per unit weight of BC (mg g^{-1}), K_F and n are indicators of adsorption capacity and intensity respectively. Maximum adsorption capacity is denoted by q_{max} (mg g^{-1}) and K_L is the Langmuir affinity parameter (L mg^{-1}). The essential characteristics of the Langmuir isotherm is expressed in terms of dimensionless separation factor (R_L).

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

The Temkin model, related to the heat of sorption is expressed by Equation (5). It assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with increase in coverage of the adsorbent surface, and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy.

$$q_{ads} = \frac{RT}{b} \ln\left(A C_e\right) \tag{5}$$

where, R, T, b and A represent the universal gas constant (8.314 J K^{-1} mol^{-1}), absolute temperature (K), heat of adsorption (J) and binding constant (L mg^{-1}) respectively. The Dubinin–Radushkevich model, describing adsorption isotherm in micropores is given by Equation (6):

$$q_{ads} = q_D \exp\left(-B_D\left[RT \ln\left(1 + 1/C_e\right)\right]^2\right) \tag{6}$$

where q_D is the monolayer adsorption capacity (mg g^{-1}). B_D is the mean free energy of sorption (mol^2 kJ^{-1}). Bonding energy for the ion-exchange mechanism (E) can be calculated from the Dubinin–Radushkevich model, using Equation (7):

$$E = \frac{1}{\left(2B_D\right)^{0.5}} \tag{7}$$

The Redlich–Peterson isotherm model incorporates three parameters into an empirical equation (Equation 8). It can be applied to represent sorption equilibrium over a wide concentration range for both homogenous and heterogeneous systems.

$$q_{ads} = \frac{q_{max} K_R C_e}{1 + a_R C_e^{\beta}} \tag{8}$$

Table 1. Proximate and ultimate analyses of TWBC300, TWBC500 and TWBC700*.

Sample	TWBC300	TWBC500	TWBC700
pH	6.25	7.17	10.21
EC (µS cm^{-1})	223	413	640
Proximate analysis			
Moisture (%)	6.13	5.34	1.57
Mobile matter (%)	38.42	27.93	10.05
Resident matter (%)	51.63	58.27	75.53
Ash (%)	3.81	8.45	12.84
Yield (%)	57.03	34.32	26.95
Ultimate analysis			
C (%)	63.54	68.07	73.63
H (%)	4.75	3.35	1.71
O (%)	27.09	24.12	7.68
N (%)	4.50	4.40	3.39
Molar H/C	0.89	0.58	0.27
Molar O/C	0.32	0.26	0.07
Molar (O + N)/C	0.38	0.32	0.11
Surface area (m^2 g^{-1})	2.28	1.57	342.22
Pore volume (cm^3 g^{-1})	0.006	ND	0.022
Pore diameter (nm)	4.323	ND	1.756
Alkaline metals (mg kg^{-1})			
Na	106	238	61
K	242	2532	226
Ca	10000	5571	4027
Mg	1312	1363	850

*[20], [17], [36].

where K_R is the constant (L mg^{-1}), a_R is empirical coefficient (mg^{-1}) and β is the exponent lies between 0 and 1.

The goodness of fit for the isotherm models was evaluated by comparing the coefficient of determination (r^2) and chi-square (χ^2). The chi-square (χ^2) values were calculated using Equation (9):

$$\chi^2 = \frac{\sum (q_{ex} - q_m)^2}{q_m} \tag{9}$$

where q_{ex} and q_m are the experimental and model calculated equilibrium capacity (mg g^{-1}) respectively.

4. Results and discussion

4.1. Biochar characterization

Morphological properties of BCs can be revealed by SEM (Figure 1-S), providing examination of structural changes taken place at different pyrolysis temperature. A breakage of original pore structure was observed indicating the escape of volatiles during pyrolysis.[25,26] Increased pyrolysis temperature has caused notable changes in pore structure as appearance of internal pores, increase in porosity and reduction in pore size. The surface area of BCs increased significantly from 2.28 to 342.22 m^2 g^{-1}. These observations are in agreement with research findings reported earlier.[22] The higher surface areas for BCs produced at 700 °C may be related to the destruction of aliphatic alkyl and ester groups and exposure of the aromatic lignin core through higher pyrolysis temperatures.[27] The largest pore volume of 0.022 cm^3 g^{-1} was obtained for TWBC700. During pyrolysis, loss of cell content mass and consequently the opening up of cellular structures create a extensive porous network and cracks resulting in a larger surface area.[25] The pore diameters ranged between 1.756 and 4.323 nm implying that mesopores which may play an essential role in many liquid-solid adsorption processes are dominant in all BCs.[25,26]

Proximate and ultimate analyses, pH and EC data are summarized in Table 1. Higher pH and EC values of TWBC700 may be due to the separation of alkali salts from organic materials at high pyrolyzing temperatures.[28] Volatile matter content decreased from ~38 to ~10% with the rise in temperature, indicating secondary decomposition at 700 °C. This was further confirmed by yield reduction of TWBC700 (27%) vs. TWBC300 (57%). Amount of fixed carbon, increased to ~76% with increased temperature of pyrolysis in TWBC700 compared with 52% in TWBC300. Similarly, BCs' ash contents increased from 3.81% (TWBC300) to 12.48% (TWBC700) with rise in temperature. This may be due to the volatilization accompanied by a relative enrichment of various inorganic components.[29] Elemental analysis data showed that carbon content increased while O and H decreased with increase in pyrolysis temperature. The increase in carbon content from 63.54 to 73.63% with the evaluated pyrolysis temperature may be due to the increase in degree of carbonization resulting polyaromatic graphene sheets.[22] However, decrease in O and H contents may be attributed to the breaking of weaker bonds in BC structure and removal of water, hydrocarbons, H_2, CO and CO_2 during carbonization.[22] Molar H/C, O/C and (O + N)/C ratios decreased with increase in pyrolysis temperature. The decrease in the H/C ratios from 0.89 to 0.27 with increase of pyrolysis temperature is associated with increase in aromaticity.[23] In addition, the decrease in the O/C and (O + N)/C ratios with increase in pyrolysis temperature indicates the reduction of O containing polar functional groups on BC surface.[27]

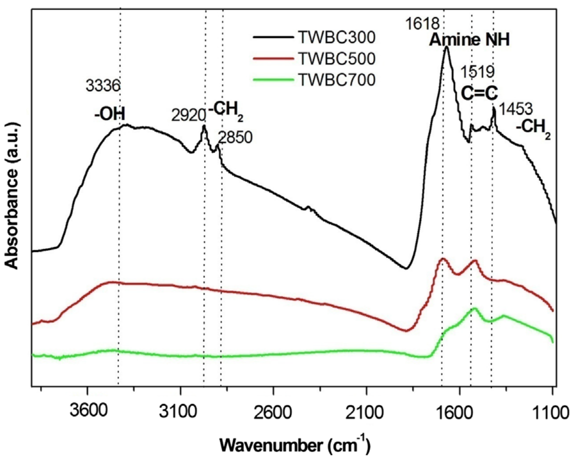

Figure 1. FT-IR spectra of TWBC300, TWBC500 and TWBC700.

The FTIR spectra for all BCs are shown in Figure 1. The band at 3336 cm^{-1} is assigned to –OH stretching and its intensity remarkably decreases accordingly in the order of TWBC300 > TWBC500 > TWBC700 due to the removal of polar –OH groups with increasing pyrolysis temperature.[22,27,30] The peaks at 2850–2920 and 1453 cm^{-1} in TWBC300 correspond to the –CH$_2$ stretching vibrations and their intensities have been diminished in both TWBC500 and TWBC700 suggesting loss of labile aliphatic groups due to high pyrolysis temperature.[31] The sharp peaks at 1618 and 1519 cm^{-1} are assigned to amine NH or –NH, and C=C stretching vibrations, respectively and the intensities of these peaks has reduced with increasing pyrolysis temperature.[22,31] The FTIR analysis further indicates that oxygen and hydrogen containing functional groups tend to eliminate with increase in pyrolysis temperature. Thus, according to experimental results from both FTIR and ultimate analysis, BCs becomes more aromatic and less polar with increasing pyrolysis temperature due to the accelerated dehydration, decarboxylation or decarbonylation processes.[23]

4.2. Adsorption edge

Adsorption capacities were evaluated at different pHs (Figure 2(a)) and it was observed that the adsorption was higher in acidic region vs. alkaline. The maximum adsorption was observed at pH 5. The adsorption capacity decreased with increase in pH, suggesting the sorption of carbofuran on TWBC is favored at low pH. In acidic medium protonation occurs to the amino groups of carbofuran molecule and the pesticide become positively charged. Therefore, the occurrence of carbofuran cations in acidic media would enhance the pesticide interaction with the negatively charged surface of the BC via electrostatic attraction, which would significantly improve sorption affinity of the BC for carbofuran.[32,33] Increase of pH results in the reduction of neutral carbofuran molecules, whereas deprotonated molecular form increases, thus creates a strong electrostatic repulsion between the negatively charged BC surface and anionic pesticide molecules.[34] In addition, by increasing pH value, the π acceptor ability would increase with protonation, resulting in weaker interaction of $\pi - \pi$ EDA between carbofuran and BC.[34] Therefore, sorption of carbofuran on TWBCs decreased on rising pH value.

4.3. Adsorption isotherms

The equilibrium adsorption isotherm is crucial to describe the interactive behavior between carbofuran and TWBCs and to determine the capacity differences among three BCs. As shown by the adsorption isotherms for all the BCs at pH 5 (Figure 3 and Figure 2-S), TWBC300 and TWBC500 show only a slight difference in sorption; indeed, TWBC700 shows rather higher sorption compared to other two. The related parameters of adsorption isotherms were also calculated by non-linear regressions and presented in Table 2. Measures of goodness of fit summarize the discrepancy between experimental

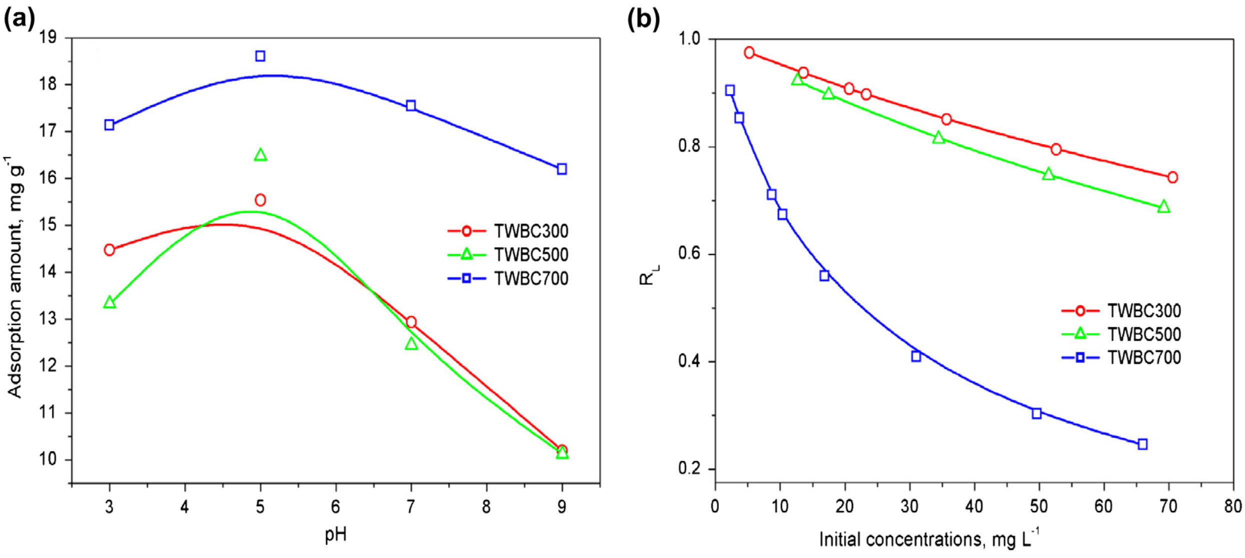

Figure 2. (a) Adsorption capacity variation with pH, (b) Langmuir separation factors for BCs at pH 5.

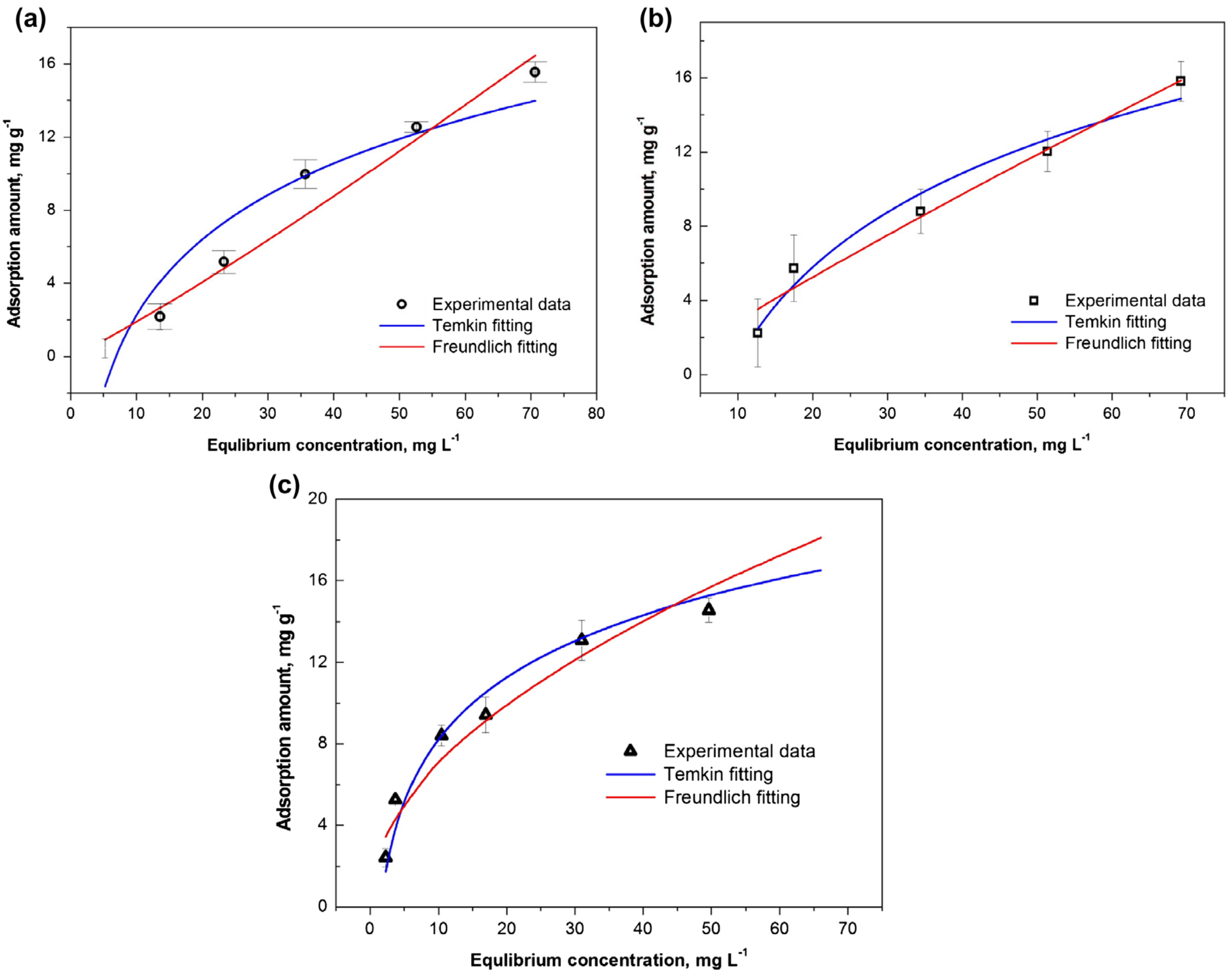

Figure 3. Freundlich and Temkin adsorption isotherms of carbofuran by TWBC300 (a), TWBC500 (b) and TWBC700 (C). Lines show the model predicted data fittings and symbols represent experimental results with standard deviations.

Table 2. Langmuir, Freundlich, Temkin, Dubinin–Radushkevish and Redlich–Peterson isotherm parameters for carbofuran adsorption onto TWBC300, TWBC500 and TWBC700 at pH 5. All parameters were calculated by non linear regression.

	Isotherm parameters										
	Langmuir		Freundlich		Temkin		Dubinin–Radushkevish		Redlich–Peterson		
Adsorbent	q_{max}(mg g^{-1})	K_L (L g^{-1})	K_F (mg g^{-1})	n	A(Lmg-1)	b	q_D(mg g^{-1})	E (kJ g^{-1})	K_R	a_R	β
TWBC300	54.719	0.0049	0.143	0.897	0.125	402	17.616	62.017	0.0064	−0.9744	0.0005
TWBC500	48.731	0.0066	0.371	1.129	0.110	339	14.706	91.287	0.0004	−0.9988	0.0002
TWBC700	22.749	0.0465	2.540	2.139	0.652	564	15.878	158.114	0.0042	−1.0000	0.0003

values and the values expected under the model. Table 3 listed the correlation coefficients (r^2) and error estimation values obtained from chi-square (χ^2) statistical function. High r^2 values and small χ^2 values imply close-fitting of the model predictions with the experimental data.[22] The isotherm models of Freundlich and Temkin with relatively higher r^2 values and smaller χ^2 values seemed to have the best fit for the carbofuran adsorption experimental data.

The K_F value for TWBC700 was significantly higher than those values of TWBC300 and TWBC500, indicating its higher capacity for carbofuran adsorption. Similarly, the Freundlich parameter n for TWBC700 was also higher than those for TWBC300 and TWBC500, indicating the higher adsorption intensity to remove carbofuran.[22] Maximum sorption capacity obtained by Langmuir equation for TWBC700 was 22.749 mg g^{-1}. Wallnut shell biomass has shown 0.19 mg g^{-1} of capacity in carbofuran adsorption. Further, It has been reported that rice straw derived activated carbon could effectively remove 135–296 mg g^{-1} of aqueous carbofuran.[16] Lower b values were given by the Temkin model for TWBC700 and TWBC500 than that for TWBC300, exhibiting that a linear decrease in the heat of adsorption resulted in greater coverage of carbofuran on the surface layer.[22]

Separation factors for all three BCs as an indication of favorability for carbofuran adsorption were determined from the Langmuir isotherm (Figure 3(b)). Typically, the $R_L > 1$ adsorption is unfavorable, $R_L = 1$ adsorption is linear, $0 < R_L < 1$ adsorption is favorable, and $R_L = 0$

Table 3. Coefficients of determination (r^2) and chi-square (χ^2) for isotherm models.

	Isotherms									
	Langmuir		Freundlich		Temkin		Dubinin–Radushkevish		Redlich–Peterson	
Adsorbent	r^2	X^2	r^2	X^2	r^2	X^2	r^2	X^2	r^2	X^2
TWBC300	0.904	3.560	0.935	2.475	0.820	4.241	0.966	11.759	0.970	5.002
TWBC500	0.971	7.283	0.975	9.259	0.972	4.065	0.903	4.661	0.974	10.079
TWBC700	0.950	1.743	0.967	1.036	0.934	1.845	0.755	2.902	0.897	4.311

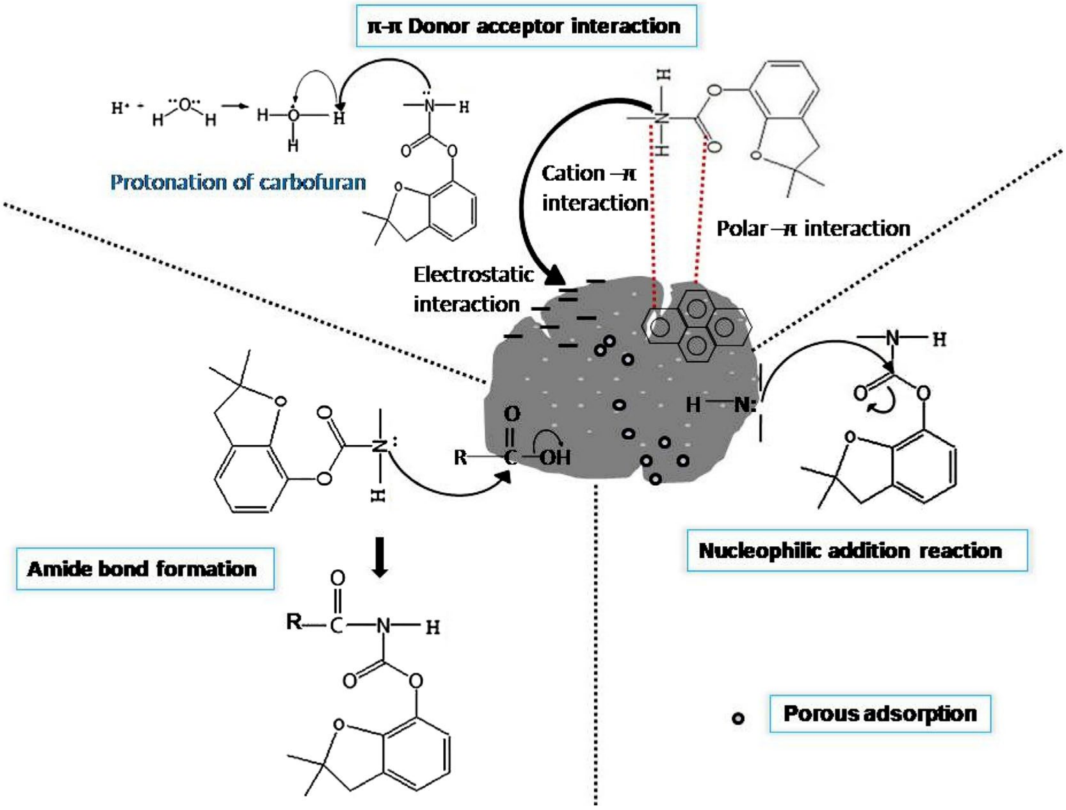

Figure 4. Possible carbofuran adsorption mechanisms.

adsorption is irreversible.[22] The R_L values were <1 (Figure 3(b)) for all sorbents used in this study, indicating that carbofuran adsorption was favorable. Also, the values of n obtained from Freundlich isotherm were greater than 1, confirming favorable adsorption. Hence it can be suggested that carbofuran adsorption by TWBC may involve heterogeneous, chemical adsorption with electrostatic interactions between pesticide molecules and the heterogeneous BC surface.

4.4. *Sorption mechanisms*

Carbofuran adsorption phenomena could be explained by several mechanisms (Figure 4). There may be π–π electron donor-acceptor (EDA) interactions between protonated aromatic ring of the carbofuran molecule and π-electron rich graphene surface of the BCs. Moreover, FTIR analysis (Figure 1) indicates the presence of $-NH_2$ (band at 1618 cm^{-1}) on the surface of BCs. Being a kind of basic group, $-NH_2$ may combine with carbofuran through acid-base interaction as carbofuran is a weak monoprotic acid.[8,35] The presence of O–H stretching vibrations of alcohols, phenols and carboxylic acid groups in the adsorbents could be assigned to the band at 3336 cm^{-1}. Such –OH groups may act as H-donor and acceptors in acidic pHs, resulting in strong H-bonding with carbofuran molecules. In addition, strong ionic bonds may exist between acidic –OH groups present in TWBCs and the basic amine and carbonyl groups of the carbofuran molecule. Besides electrostatic interactions, ion exchange and hydrophobic interactions could be other possible mechanism. Further, carbonyl carbon (C=O) of the carbofuran molecule has high tendency to act as an electrophile in acidic medium. Such an elecrophile is capable of attacking on electron rich O atom of the phenolic OH group leading strong chemical interactions. Similarly, protonated amine group of the carbofuran molecule also can attack either on ortho or para positions of phenolic aromatic ring, giving rise to electrophilic addition reactions (Figure 4).

5. Conclusions

Infused tea residue derived BCs produced at high temperature showed the maximum carbofuran removal at pH 5. The sorption equilibrium data obtained from batch studies were best described by Freundlich and Temkin isotherm models; indicating a chemisorption dominating mechanism. Moreover carbofuran adsorption is a favorable process with electrostatic attractions between carbofuran molecules and BC surface. Also we suggest an electrophillic addition reactions and amide bond formation as possible mechanisms for carbofuran removal by TWBCs. Hence, the BC prepared from disposable tea waste is a promising adsorbent for carbofuran.

Disclosure statement

No potential conflict of interest was reported by the authors.

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