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Comparative study of carbon black and activated carbon adsorbents for removal of carbofuran from aqueous solution

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ABSTRACT

Three commercial carbon samples of carbon black, namely Black Pearl 2000 (BP 2000), extruded activated carbon (EAC), and granular activated carbon (GAC), were evaluated as adsorbents for the removal of carbofuran from water. The specific surface area and micropore volume of the adsorbents were studied by BET measurements and *t*-plot, respectively. Batch experiments were conducted to examine the effects of the adsorbents as a function of the initial concentration of carbofuran, adsorption contact time, and solution pH. As per the results, the equilibrium uptake for carbofuran on all adsorbents increased with an increase in the initial carbofuran concentration in solution, and the removal potential of carbofuran followed the order BP 2000 > GAC > EAC. The amount of carbofuran uptake at equilibrium was applied to investigate the suitability of the Langmuir, Freundlich, and Temkin models. The results indicated that the equilibrium data obey the Langmuir isotherm model better than Freundlich, and Temkin models. The adsorption kinetics data were used to compare the feasibility of the two models: pseudo-first-order kinetic and pseudo-second-order kinetic. The data fit the pseudo-second-order model well. The ranking order of adsorbents in terms of adsorption kinetic constants was as follows: BP 2000 > EAC > GAC. Thermodynamics studies were carried out and various thermodynamics parameters such as standard free energy changes (ΔG), standard enthalpy change (ΔH), and standard entropy change (ΔS) were calculated. The values of ΔG were found as negative, which confirms the spontaneous nature of the adsorption processes. The results of the study supported the usability of BP 2000, EAC, and GAC as promising adsorbents for carbofuran adsorption.

Keywords: Activated carbon; Carbon black; Carbofuran removal; Adsorption isotherm; Thermodynamics

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1. Introduction

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl *N*-methyl carbamate) is a derivative of the broad spectrum insecticide carbamate [1]. It is extensively used as an agricultural insecticide for controlling insects and nematodes in various crops such as rice, sugarcane, maize, potato, tobacco, soybean, and vegetables [1,2]. Since it is highly water soluble (351 mg/L), it can easily migrate from soil and surface runoff [3]. The persistence of carbofuran in the environment (half-life is 5.1 weeks at pH 7.0 in water) not only causes risk to humans, plants, and animals [4], but also poses a severe threat, particularly for fish and mammals, because of its high toxicity [5]. The toxicity of carbofuran has been examined in rats and mice, with lethal dose 50 values of 11 mg/kg [6] and 2 mg/kg body weight [7], respectively. Exposure to carbofuran causes negative effects on human reproductive system [8] and this pesticide has the potential to inhibit the function of acetylcholinesterase [5]. According to the World Health Organization, the acceptable maximum concentration of carbofuran in drinking water is 3.0 μg/L [9], and the United States Environmental Protection Agency stipulates a maximum concentration of 40.0 μg/L for carbofuran [10].

For these reasons, it is essential to develop an effective treatment technology for maintaining water quality. Thus far, several methods have been adopted to remove carbofuran from drinking or wastewater, such as ozone [11], microwave-assisted granular activated carbon/zerovalent iron/H_2O_2 system [1], microwave-assisted H_2O_2 process [2], Fenton process [4], photocatalytic decomposition [12] and adsorption [13]. Among these methods, adsorption has been extensively and successfully employed because of several advantages such as cost-effectiveness, availability of adsorbents, and high efficiency [14,15]. In addition, effective changes in the properties of adsorbents may increase their potential for use as adsorbents; this aspect has been attracting interest from researchers recently [16]. A change in the material surface area and functional groups can accelerate the extent and strength of adsorbent capacity [17].

Black Pearl 2000 (BP 2000) is steam-activated carbon black produced by a furnace process using heavy aromatic oil as the feedstock [18]. Different from the feedstock of activated carbon, that of carbon black is thermally cracked by an oil furnace process, followed by cooling and collection of commercial carbon black [17]. As carbon black is prepared from hydrocarbon, it contains a significant amount of hydrogen and oxygen [19]. Similar to other carbon, carbon black also contains acidic and basic groups, which can participate in adsorption [19,20]. Extruded activated carbon (EAC) and granular activated carbon (GAC) have a high porous structure and surface area [17]. Activated carbon is extensively utilized in adsorption studies because its high porous structure and surface area can accumulate a high concentration of contaminant molecules [21].

This study describes the adsorption performance of three adsorbents—BP 2000, EAC, and GAC—for the removal of carbofuran. The surface properties of adsorbents were studied. Batch experiments were carried out to test the effect of different reaction parameters on the adsorption of carbofuran such as: adsorption contact time, initial carbofuran concentration, and solution pH. Isotherm, kinetics, and thermodynamics studies were also performed. However, in the literature, the adsorption of carbofuran has been reported using different adsorbent materials, and most of them exhibit poor adsorption capacity [8,13,21]. The present study has been intended to explore and compare the effectiveness of BP 2000, EAC, and GAC as adsorbents for the carbofuran removal.

2. Materials and methods

2.1. Adsorbate

Technical-grade carbofuran (98% purity) was purchased from Sigma Aldrich (USA) and stored in a refrigerator at 4°C. A carbofuran working solution was prepared prior to the start of the experiment, and water was deionized using a Milli-Q water purification system (USA) before use in experiments.

2.2. Adsorbents

All adsorbents were commercially available and used without any further purification. BP 2000 and GAC (Norit GAC 830 plus M-1666) were obtained from Cabot Corporation (USA). BP 2000 contains fine particles of furnace process steam-activated carbon black, and GAC (0.42–2.36 mm particles) is acid-washed steam-activated selected grade coal. EAC or extruded pellet is activated charcoal (Norit Row 0.8 Supra) supplied by Sigma Aldrich (USA).

2.3. Characterization and properties of adsorbents

For better understanding the mechanism related to adsorption, it is essential to investigate the physical and chemical properties of the adsorbents. Hence, the surface morphology of the adsorbents was studied. Nitrogen adsorption–desorption isotherms were evaluated to obtain the specific surface area, micropore volume, and total pore volume. The analysis was conducted at −196˚C using a surface area and porosity analyzer (Micromeritics, Tristar II 3020, USA); prior to analysis, the adsorbents were activated by evacuation at 150˚C for 12 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and micropore volume data were analyzed by the t-method. The surface morphology of the absorbents was investigated by scanning electron microscopy (SEM, JSM-6701F, JEOL, Japan).

2.4. Fourier transform infrared study

To compare the changes of functional groups on the surface, FTIR spectra of carbofuran, unused BP 2000, and BP 2000 after the adsorption of carbofuran were recorded on a spectrometer (Jasco FTIR-4100, maximum resolution: 0.9 cm^{-1}) in the range of 650–3,000 cm^{-1}.

2.5. Determination of pH_{pzc}

Typically, potentiometric titration and batch equilibrium are the techniques employed to determine the point of zero charge (pH_{pzc}) [22]. In this study, the latter was adopted, as it is easy to conduct. To obtain pH_{pzc}, 5.0 mg of BP 2000 was added in a 50.0 ml 0.1 M $NaNO_3$ (inert electrolyte) solution in 100 ml glass bottles. HNO_3 (0.01 M) or NaOH (0.01 M) was used each time to adjust the desired pH values from 2.0 to 12.0 at every 1.0 interval. The sample was allowed to equilibrate for a sufficient time in a shaking incubator at 25˚C and 150 rpm. After attaining equilibrium, the sample was filtered, and the final pH was measured.

2.6. Batch equilibrium studies

For adsorption studies, the adsorbents were placed in a desiccator and vacuum dried overnight at 110˚C before use. Adsorption tests were performed in 100 mL glass bottles in which 5.0 mg of adsorbent was dissolved in 50.0 mL water at an initial carbofuran concentration ranging from 50.0 to 200.0 mg/L. Unless otherwise specified, all experiments were conducted at pH 7.0 and 25˚C. The shaker was adjusted at 150 rpm, and samples were passed through nylon syringe filters (0.2 μm, Whatman, UK) at predetermined times to analysis using a UV–vis spectrophotometer (Scinco, S3100, Korea) at 272 nm. The adsorption kinetic data were verified using pseudo-first-order and pseudo-second-order kinetic equations [23,24] and maximum adsorption capacity was calculated using Langmuir adsorption isotherm [25]. For thermodynamics studies, the adsorption process was further carried out at 35 and 45˚C. Each experiment was performed in triplicate, and the average value was applied to determine the amount of adsorption.

The effect of pH on the adsorption of carbofuran was examined by varying the pH from 2.0 to 8.0. To adjust the pH of a solution, HCl (0.1 M) or NaOH (0.1 M) was used, and the results were monitored using a pH meter (Accumet Basic, AB 15 plus, USA). The effect of pH was studied at a carbofuran concentration of 100.0 mg/L. Carbofuran rapidly hydrolyzes at high pH (half-life is 1.2 h at pH 10.0 in water) [4]; therefore, the effect of pH over 8.0 was not evaluated in this study.

The amount of adsorbed carbofuran at time t, q_t (mg/g), over three adsorbents was calculated by the mass balance equation [26]:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

Here C_0 (mg/L) and C_t (mg/L) represent the liquid-phase concentrations of the carbofuran at time = 0 and t, respectively. V (L) is the volume of the solution, and W (g) is the amount of adsorbent used.

3. Results and discussion

3.1. Characterization and properties of adsorbents

Fig. 1(a), (b), and (c) show SEM images of BP 2000, EAC, and GAC, respectively. BP 2000 exhibited fine particles, with an average particle size of approximately 50–70 nm. Therefore, BP 2000 has good potential for the adsorption of carbofuran as compounds of a small particle size (BP 2000) exhibit a high specific surface area and high adsorption capacity [18]. On the other hand, the particles of EAC and GAC were comparatively greater than those of BP 2000. However, their surfaces were rough containing sufficient pores; hence, they could also exhibit high potential for the adsorption of carbofuran [13]. Table 1 shows the BET analysis data; the specific surface areas of BP 2000, EAC, and GAC were 1,216, 702, and 659 m^2/g, respectively; the higher value of BP 2000 indicates better feasibility for the adsorption of carbofuran. The higher total pore volume (2.58 cm^3/g) of BP 2000 is also indicative of it being an efficient adsorbent for the removal of carbofuran [26].

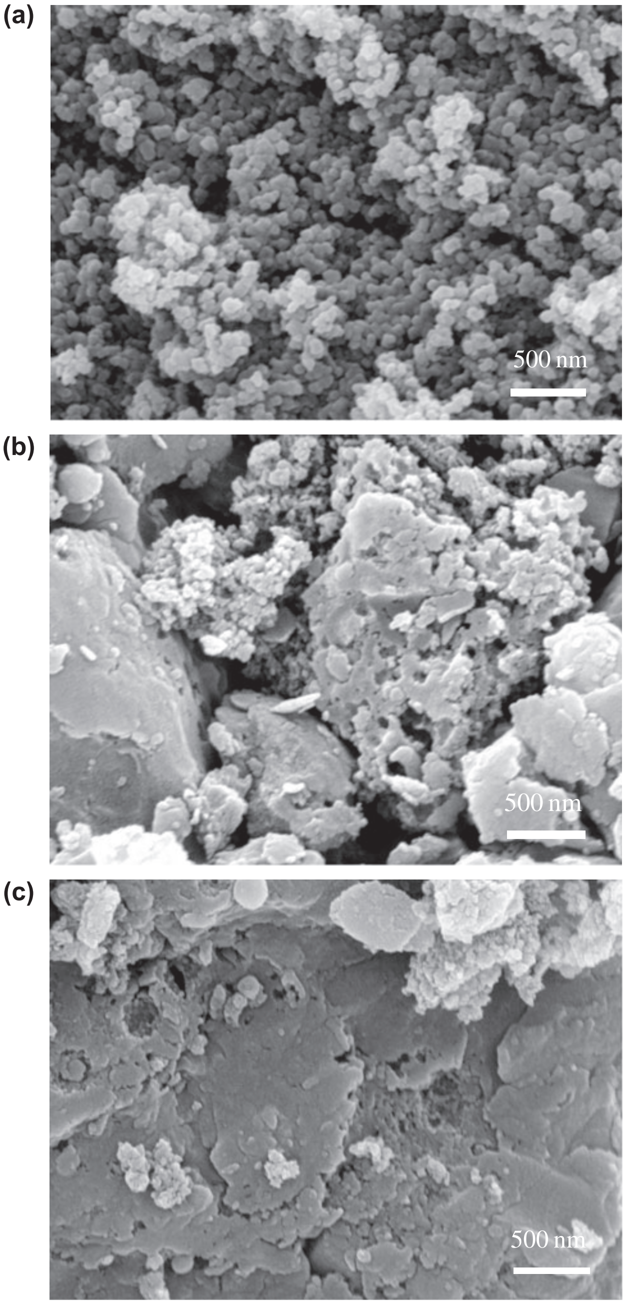

Fig. 1. Scanning electron microscopy (SEM) images: (a) BP 2000, (b) EAC, and (c) GAC.

3.2. Fourier transform infrared study

Fig. 2 shows the FTIR spectrum of BP 2000 after the adsorption of carbofuran; three new peaks were observed at 1,715, 1,464, and 1,226 cm^{-1}, which are attributed to C=O stretching vibration, C–O stretching, and C–N stretching, respectively [27]. No clear changes were observed in the FTIR spectra of EAC and GAC after carbofuran adsorption; hence, their spectra have not been shown in this study.

3.3. Effect of adsorption contact time and initial carbofuran concentration

The time course to attain adsorption equilibrium was studied at 25°C, and various carbofuran concentrations ranging from 50.0 to 200.0 mg/L (Fig. 3). At the initial stage of adsorption, the rate of carbofuran uptake was rapid, but it gradually slowed with time and finally stopped after which no significant removal was observed. In addition, the time required to attain adsorption equilibrium fluctuated among adsorbents. BP 2000 exhibited rapid adsorption of carbofuran, and equilibrium was achieved within ~5.0 min. The rapid adsorption of carbofuran may be caused by the chemical interactions occurring on the external surface of BP 2000 [13]. On the other hand, adsorption was comparatively slower (up to ~480.0 min) in the case of EAC, after which no further adsorption was observed. Moreover, GAC exhibited the longest time to reach equilibrium, where molecular diffusion took up to ~4,320.0 min. This is probably caused by the fact that when the external surface is saturated with carbofuran, it may also enter the pores of the particles and get adsorbed on the interior surface [13]. However, a similar trend of such adsorption by GAC has been reported previously in the case of GAC application for the control of pollutants such as p-nitrophenol and o-nitrophenol [28].

From Fig. 3 it can be also observed that the equilibrium adsorption capacities of all adsorbents increased with increasing carbofuran concentration in solution. When the concentration of carbofuran increased from 50.0 to 200.0 mg/L, carbofuran consumption by BP

Table 1
Textural properties of BP 2000, EAC, and GAC adsorbents used for the adsorption of carbofuran

Adsorbent	BET specific surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)
BP 2000	1,216	0.210	2.58
EAC	702	0.221	0.43
GAC	659	0.161	0.56

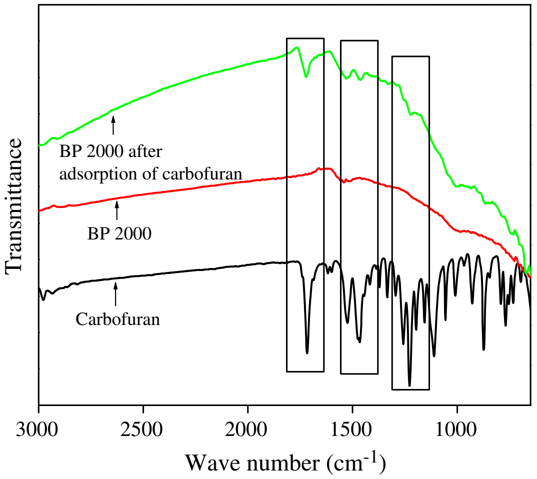

Fig. 2. Comparison of the Fourier transform infrared (FTIR) spectra of carbofuran, BP 2000, and BP 2000 after the adsorption of carbofuran.

2000 and GAC increased from 346.2 to 521.1 mg/g and from 300.0 to 464.3 mg/g, respectively. When the initial carbofuran concentration in solution increased from 50.0 to 200.0 mg/L, the carbofuran consumption increased from 176.0 to 264.0 mg/g for EAC. Moreover, when the initial carbofuran concentration increased from 150.0 to 200.0 mg/L, carbofuran adsorption by EAC increased only slightly (250.0–264.0 mg/g). Overall, the maximum consumption values of 521.1, 264.0, and 464.3 mg/g for carbofuran by BP 2000, EAC, and GAC, respectively, were observed at an initial carbofuran concentration of 200.0 mg/L. This phenomenon can be explained by the fact that a high initial concentration of 200.0 mg/L introduces a high driving force to overcome the mass transfer resistance of solutes between the aqueous and solid phases [29]. Therefore, the comparative efficiencies of the adsorbents for the removal of carbofuran follow the order of BP 2000, GAC, and EAC.

The highest consumption by BP 2000 was reasonably caused by its smaller particle size (average particle size of 50–70 nm) and porous structures, which lead to a higher specific surface area. Notably, this adsorbent contains a substantial amount of macropores, mesopores, and micropores. Mesopores (2–50 nm diameter) and macropores (exceeding a diameter of 50 nm) exert a significant influence on the adsorption of larger organic solutes, because these solutes have suitably sized particles that can easily pass through the adsorbent pores [18]. In contrast, micropores are suitable for the adsorption of smaller solutes. In addition, the primary particles of BP 2000 are spatially arranged as compact aggregates, which possibly exert a significant influence on its higher adsorption capacity [18]. As compared to BP 2000 and GAC, EAC exhibited a lower performance for the adsorption of carbofuran, which is probably related to its unfavorable surface properties for high carbofuran uptake.

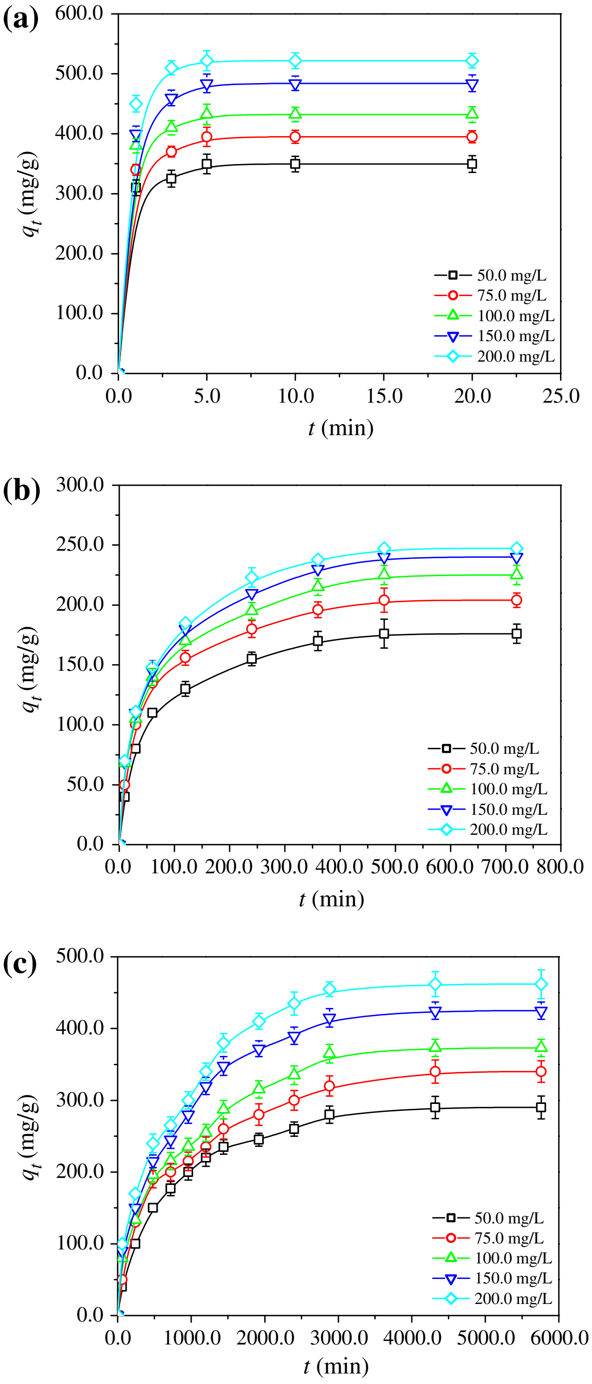

Fig. 3. Effect of contact time and initial carbofuran concentration on the adsorption of carbofuran over three adsorbents at 25°C: (a) BP 2000, (b) EAC, and (c) GAC. Error bars represent the mean standard deviation, and data points without error bars are shown within symbols.

The comparatively low total pore volume (0.43 cm^3/g) and high micropore volume (0.221 cm^3/g) might affect the limited binding of carbofuran. GAC was highly suitable for high carbofuran adsorption, probably because of its higher specific surface area (659 m^2/g) and total pore volume (0.56 cm^3/g). Other than the above-mentioned factors, the variation in activation procedures and raw materials of activated carbon could also play an important role in this regard [17].

3.4. Effect of solution pH on carbofuran adsorption

Adsorption uptake varies with the change in solution pH because pH affects the surface charge of the adsorbents and ionization state of the solutes [13,30]. Fig. 4 plots equilibrium adsorption capacities for carbofuran by adsorbents as a function of pH (studied from pH 2.0 to 8.0) in a solution with an initial carbofuran concentration of 100.0 mg/L at 25℃. The adsorption of carbofuran by BP 2000 was not significantly affected by the change in the solution pH. More specifically, BP 2000 showed a similar adsorption trend throughout the pH range studied. With an increase in pH from 2.0 to 8.0, the equilibrium adsorption capacity of 5.0 mg BP 2000 in a 50.0 mL solution reduced only from 437.00 to 433.00 mg/g. This might be caused by large pH_{pzc} values range of BP 2000 from 2.0 to 12.0 (figure not shown). BP 2000 is observed in its neutral (net surface charge is zero) form throughout the pH range. On the other hand, carbofuran possibly exists in its non-dissociated form in solution at pH 7.0 [8], with a pK_a of 11.65 ± 0.46 [31]. Hence, there is no sufficient electrostatic interaction of carbofuran at this pH. However, when the pH of solution decreases, carbofuran probably becomes more positively charged than pH 7.0 or 8.0 [27], but BP 2000 still exists to be neutral; therefore, no significant interaction may occur even at lower pH because of the absence of electrostatic interactions. Thus, it is reasonable to state that BP 2000 may not show a high variation of carbofuran uptake with change in pH.

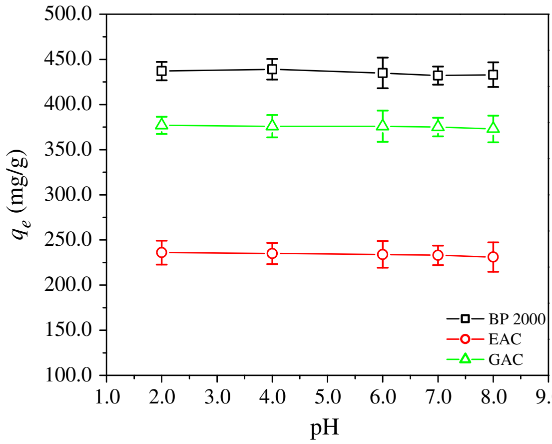

Fig. 4. Effect of pH on carbofuran adsorption over three adsorbents at 25℃. Error bars represent the mean standard deviation, and data points without error bars are shown within symbols.

On the other hand, the uptake of carbofuran by EAC and GAC did not significantly vary on changing the pH from 2.0 to 8.0, because the functional groups (carbonyl and hydroxyl) present on the surface of activated carbon tend to be more deprotonated at a higher pH than low pH [32]. As carbofuran is mostly present in its neutral form at pH 7.0 or 8.0, no effective electrostatic interactions exist between carbofuran and EAC or GAC throughout the entire pH range [8]. This observation is identical to the characteristics of carbofuran adsorption in other studies. It has been reported that the adsorption of carbofuran by banana stalk activated carbon slightly decreases from 65.33 to 63.53 mg/g with increasing pH from 2.0 to 12.0 [13]. On the other hand, pH changes have not been reported to significantly affect the removal of carbofuran by date seed activated carbon [8]. In a previous study, 5% carbofuran adsorption is reduced using waste slurry caused by an increase in pH from 2.0 to 8.0 [32].

3.5. Adsorption isotherm studies

The adsorption process was tested at 25℃ for different initial carbofuran concentrations (50.0, 75.0, 100.0, 150.0, and 200.0 mg/L) and the equilibrium data were used to fit with the three common isotherm models: Langmuir, Freundlich, and Temkin. The linear form of the Langmuir model [25] is represented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 K_a} \qquad (2)$$

Here C_e (mg/L) represents the equilibrium carbofuran concentration in solution, q_e (mg/g) is the amount of carbofuran adsorbed at equilibrium, Q_0 (mg/g) is the Langmuir constant (maximum adsorption capacity), and K_a (L/mg) is the Langmuir constant. The linear form of the Freundlich isotherm [33] model is represented as follows:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \qquad (3)$$

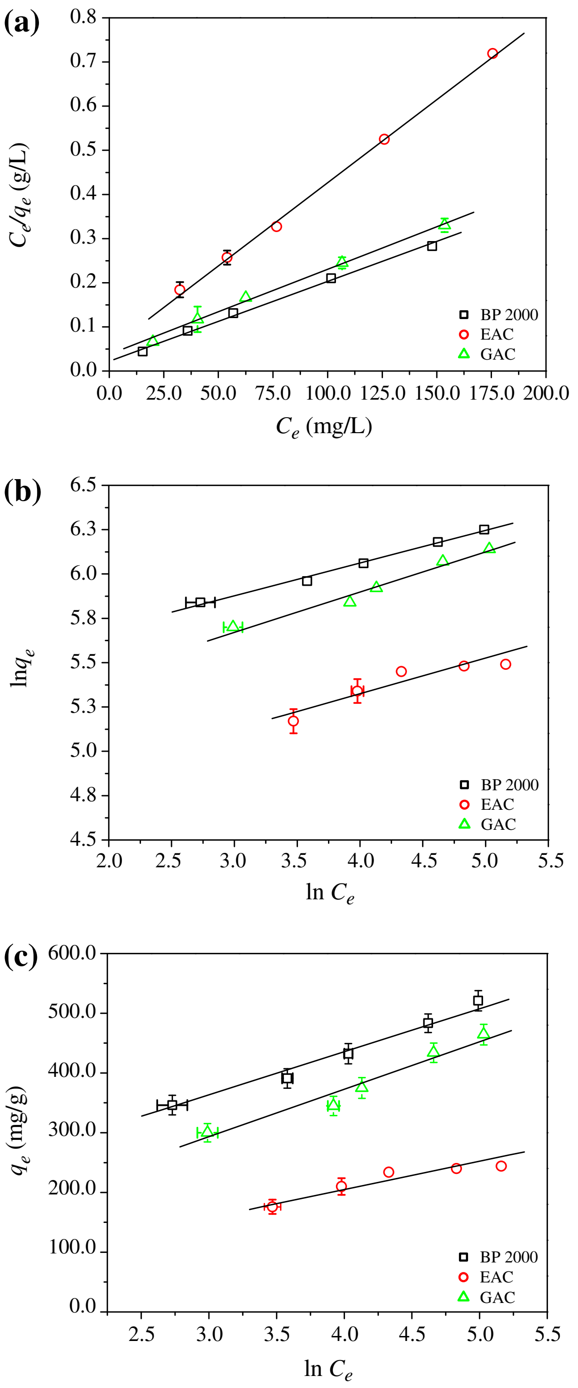

Fig. 5. Adsorption isotherms for the adsorption of carbofuran over three adsorbents at 25°C: (a) Langmuir isotherm plot, (b) Freundlich isotherm plot, and (c) Temkin isotherm plot. Error bars represent the mean standard deviation, and data points without error bars are shown within symbols.

Table 2
Langmuir, Freundlich, and Temkin isotherm parameters for the adsorption of carbofuran over BP 2000, EAC, and GAC at 25°C

Parameters	BP 2000	EAC	GAC
Langmuir			
K_a (L/mg)	0.074	0.046	0.053
Q_0 (mg/g)	561.79	294.11	515.46
R^2	0.996	0.995	0.995
Freundlich			
K_F (mg/g(L/mg)$^{1/n}$)	202.35	85.11	148.41
n	5.40	4.46	4.47
R^2	0.992	0.957	0.975
Temkin			
A (L/g)	4.8	1.33	1.58
B	78.07	49.26	83.27
R^2	0.983	0.975	0.959

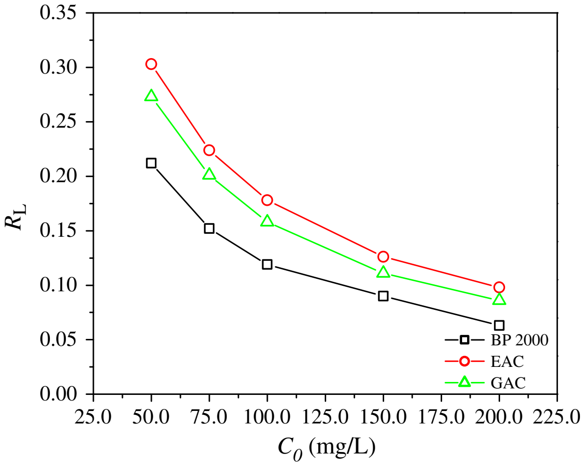

Fig. 6. Effect of the initial carbofuran concentration on the separation factor R_L for adsorbents.

Here K_F (mg/g (L/mg)$^{1/n}$) and $1/n$ are two Freundlich model constants, which represent relative adsorption capacity of the adsorbent and adsorption intensity, respectively.

The linear form of the Temkin isotherm [34] is described as follows:

$$q_e = B \ln A + B \ln C_e \tag{4}$$

Table 3
Kinetics models parameters for the adsorption of carbofuran over three adsorbents at 25˚C a d various initial carbofuran concentrations

Adsorbent concentration (mg/L)	Pseudo-first-order kinetic model					
	BP 2000		EAC		GAC	
	K_1 (g/mg min)	R^2	K_1 (g/mg min)	R^2	K_1 (g/mg min)	R^2
50.0	0.872	0.787	0.0061	0.918	0.0009	0.977
75.0	0.824	0.845	0.0076	0.959	0.0010	0.976
100.0	0.906	0.825	0.0081	0.945	0.0011	0.954
150.0	0.946	0.920	0.0081	0.979	0.0014	0.956
200.0	1.200	0.952	0.0085	0.985	0.0016	0.926
	Pseudo-second-order kinetic model					
	K_2 (g/mg min)	R^2	K_2 (g/mg min)	R^2	K_2 (g/mg min)	R^2
50.0	0.042	0.998	1.61×10^{-4}	0.990	9.0×10^{-6}	0.982
75.0	0.031	0.997	1.49×10^{-4}	0.990	8.6×10^{-6}	0.977
100.0	0.026	0.998	1.30×10^{-4}	0.990	7.5×10^{-6}	0.975
150.0	0.020	0.997	1.28×10^{-4}	0.992	7.0×10^{-6}	0.977
200.0	0.018	0.998	1.27×10^{-4}	0.991	5.9×10^{-6}	0.975

Here $B = RT/b$, b indicates the Temkin constant, which depends on the heat of sorption (J/mol), A indicates the Temkin isotherm constant (L/g), R indicates the gas constant (8.314 J/mol K), and T indicates the absolute temperature (K).

For the best fitting of data, the linear regression method was applied, and the correlation coefficients (R^2) were calculated for comparing the degree of accuracy of the models. Fig. 5(a) shows the plot of specific adsorption (C_e/q_e) of carbofuran against the equilibrium concentration (C_e; Langmuir model) over three adsorbents. Fig. 5(b) shows the plot of $\ln q_e$ against $\ln C_e$ (Freundlich model), and Fig. 5(c) shows the plot of $\ln C_e$ against q_e (equilibrium adsorption; Temkin model).

The adsorption isotherm parameters determined from the linear models are summarized in Table 2. The adsorption of carbofuran can be demonstrated very well by the Langmuir model because the R^2 value was higher than those obtained from the Freundlich and Temkin models: 0.996, 0.995, and 0.995 for BP 2000, EAC, and GAC, respectively. The higher R^2 value indicates that the adsorption is favorable because the surface active sites of adsorbents may be homogeneously distributed with equal activation energy [13]. The maximum adsorption capacity (Q_0) values of 561.79, 294.11, and 515.46 mg/g were obtained for BP 2000, EAC, and GAC, respectively. From these values, the adsorption efficiency of BP 2000 for carbofuran is 1.08 and 1.91 times higher than those of GAC and EAC, respectively, suggesting the higher effectiveness of BP 2000 for the adsorption removal of carbofuran. Q_0 has been previously reported to be significantly dependent on the surface properties of adsorbents [35]. More specifically, when the pore volume or specific surface area increases, the uptake of solutes also increases, thereby increasing Q_0. The Langmuir constant (K_a) follows the order of BP 2000 > GAC > EAC, which confirms the most favorable adsorption by BP 2000.

The separation factor R_L, a dimensionless constant, was calculated to describe the characteristics of the Langmuir isotherm model [36]:

$$R_L = \frac{1}{1 + K_a C_0} \tag{5}$$

Fig. 6 shows the R_L values at various initial carbofuran concentrations for different adsorbents. An R_L value between 0.0 and 1.0 is indicative of favorable adsorption on all three adsorbents [13]. Notably, the R_L value decreased with increasing concentration from 50.0 to 200.0 mg/L, suggesting that adsorption is more favorable at a higher initial carbofuran concentration. Therefore, it can be inferred that adsorption is the most effective on BP 2000 and is the highest as the separation factor R_L follows the order of BP 2000 < GAC < EAC. This result also supports the maximum adsorption capacity (Q_0) of the adsorbents (BP 2000 > GAC > EAC).

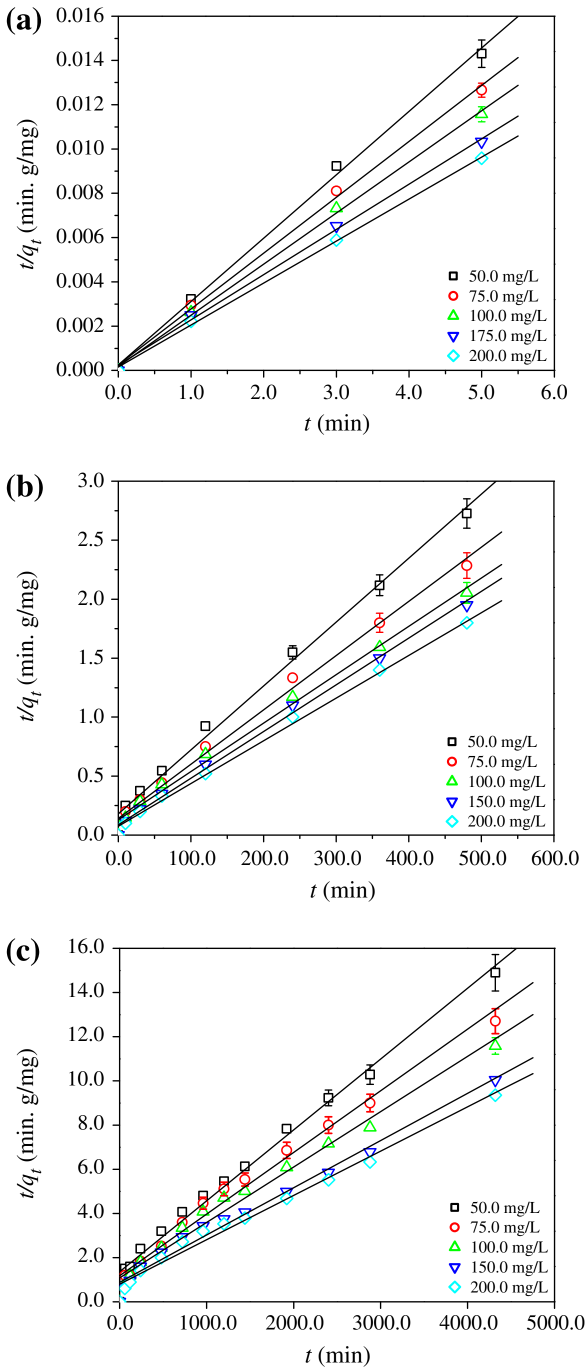

Fig. 7. Plots of pseudo-second-order kinetics for the adsorption of carbofuran over three adsorbents at 25˚C: (a) BP 2000, (b) EAC, and (c) GAC. Error bars represent the mean standard deviation, and data points without error bars are shown within symbols.

A higher Freundlich constant K_F value is indicative of higher adsorption capacities of BP 2000 with easy uptake [28]. The adsorption capacity of EAC is the lowest as K_F has the lowest value (Table 2). A similar trend was observed in the case of adsorption intensity (n); however, the value was observed to be quite high for separation in all cases.

The adsorption capacity of carbofuran by other adsorbents was compared; BP 2000 exhibited the highest capacity. The adsorption capacities of rice straw activated carbon [37] and waste slurry [32] for carbofuran are 296.52 and 208.30 mg/g, respectively. However, for commercial activated carbon, adsorption capacity decreases drastically: 97.10 mg/g for CAC-F200 [38] and 96.15 mg/g for GAC-F300 [21]. The low adsorption performance (0.00226 mg/g) was obtained in case of the use of bentonite [39].

3.6. Adsorption kinetics studies

The study of kinetics is considered important since it deals with the process efficiency. In literature, the adsorption kinetics have been studied using various kinetic models, among all the models, pseudo-first-order [23] and pseudo-second-order kinetics models have been widely used [23,24]. To get kinetics information, the adsorption experiments were conducted at 25˚C for different initial concentrations of carbofuran (50.0, 75.0, 100.0, 150.0, and 200.0 mg/L) and the experimental data were treated to the pseudo-first-order and pseudo-second-order kinetic models.

The pseudo-first-order kinetic model is like:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

Here q_t (mg/g) and q_e (mg/g) are the amount adsorbed at time t and equilibrium, and k_1 is the first-order-kinetic constant. The values of k_1 were obtained from the slope, plotting $\ln(q_e - q_t)$ against t. The correlation coefficients (R^2) values were measured for the straight lines. The values of k_1 are given in Table 3 along with the corresponding R^2 values. The results revealed that, the first-order model data show poor linearity because the R^2 values are low, indicating that this model does not fit well [23].

The kinetics data were treated again to the pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

Here k_2 is the pseudo-second-order kinetic constant. The values of k_2 were calculated from the slope ($1/q_e$) and intercept ($1/k_2q_e^2$), when the t/q_t was plotted against t (Fig. 7). The value of k_2 and their corresponding R^2 values are displayed in Table 3. As

Table 4
Maximum adsorption capacity and thermodynamics parameters for the adsorption carbofuran over three adsorbents at different temperatures (25, 35, and 45˚C)

Adsorbents	Temp. (˚C)	Q_0 (mg/g)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
BP 2000	25	561.79	−24.02	9.71	112.57
	35	584.79	−25.07		
	45	591.71	−26.13		
EAC	25	290.69	−22.92	−27.85	−14.93
	35	283.28	−22.89		
	45	271.00	−22.68		
GAC	25	515.46	−23.26	8.72	106.85
	35	529.10	−24.32		
	45	543.47	−25.39		

can be seen, the data are in good agreement with the second-order kinetic model as the R^2 values are close to 1 ($R^2 \geq 0.975$) [40]. Thus, the kinetic data better represent the pseudo-second-order kinetic model as the R^2 values are relatively higher in pseudo-second-order kinetic model than the first-order kinetic model [40]. The result also suggests that the kinetic constant values for carbofuran adsorption by BP 2000 are higher than EAC and GAC, similar to adsorption quantity. The higher kinetic constant is an indication of higher adsorption rate [23]. This proves that BP 2000 is the most effective adsorbent for carbofuran removal.

3.7. Thermodynamics studies

Temperature is a crucial parameter in adsorption process since the change of temperature may affect adsorption process performance by changing the adsorbents capacity to uptake adsorbate [40]. Due to the increase in temperature from 25 to 45˚C, the Q_0 value of BP 2000 and GAC were increased from 561.79 to 591.71 mg/g and from 515.46 to 543.47 mg/g, respectively, whereas Q_0 value was decreased in case of EAC, 294.11 mg/g at 25˚C to 277.77 mg/g at 45˚C (Table 4). The value of Q_0 increases with the increase in temperature suggesting the endothermic nature of the process [40] and if the Q_0 value favors the lower solution temperatures, then this indicates that the adsorption process is exothermic [41]. When performing thermodynamics studies, it is very important to consider various parameters, such as, change in standard free energy (ΔG), change in standard enthalpy (ΔH), and change in standard entropy (ΔS). The ΔG values were calculated as follows [23,24,42]:

$$\Delta G = -RT \ln K_a \tag{8}$$

Here R (8.314 J/mol K), T, and K_a are the gas constant, the absolute temperature (K), and Langmuir constant (L/mol), respectively. The values of ΔH and ΔS were measured using Van't Hoff's equation [23,24,42]:

$$\ln K_a = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

The plots of $\ln K_a$ vs. $1/T$ gave linear lines, and the values of ΔH and ΔS were calculated from the (–slope × R) and (intercept × R), respectively. The values of ΔG, ΔH, and ΔS are displayed in Table 4. The ΔG values were found to be negative for all adsorbents in this study. The negative value of ΔG suggests the spontaneous nature of the adsorption [43]. The positive value of ΔH for carbofuran adsorption by BP 2000 and GAC corresponds to the endothermic nature of the adsorption process [40]. The endothermic adsorption may be attributed to the strong interaction between pre-adsorbed water and the adsorbent than that of interaction between carbofuran and adsorbents [23,24]. The positive value of ΔS signifies increased randomness at the solid/solution interface during adsorption of carbofuran on the adsorbent surface [40]. The values of ΔG for the case of EAC were found to be –22.92 at 25˚C and –22.70 at 45˚C, which illustrates that the adsorption of carbofuran by EAC became less favorable at higher temperatures [44]. The negative ΔH confirms exothermic nature of the adsorption [43] and negative ΔS indicates the decreased randomness at the solid/solution interface during the adsorption process [43].

4. Conclusion

The potential of BP 2000, EAC, and GAC as adsorbents for the removal of carbofuran from an aqueous solution was investigated. The characteristics of adsorbents were studied using nitrogen adsorption–desorption isotherms, SEM images, and FTIR analyses. The effects of various reaction parameters such as contact time, initial carbofuran concentration, and solution pH on adsorption of carbofuran were examined. Equilibrium data were applied to the Langmuir, Freundlich, and Temkin isotherm models and the data were best interpreted by the Langmuir isotherm. The maximum adsorption capacities of 561.79, 294.11, and 515.46 mg/g were observed for carbofuran at 25°C on BP 2000, EAC, and GAC, respectively, suggesting that BP 2000 is the most effective adsorbent material for the removal of carbofuran. The adsorption kinetics data were analyzed using pseudo-first-order and pseudo-second-order kinetic model. The result showed that, the adsorption kinetics data were more accurately described by the pseudo-second-order kinetic model than the pseudo-first-order-kinetic model. The kinetics constant values for carbofuran adsorption were found higher for BP 2000 than EAC and GAC, similar to adsorption quantity. All ΔG values were obtained as negative, which means that the uptake of carbofuran by adsorbents was a spontaneous process. The ΔH and ΔS value by BP 2000 was found to be 9.71 kJ/mol and 112.57 J/mol K, respectively, indicating endothermic nature of the process and increased randomness at solid/solution interface for adsorption of carbofuran. From this study, it was concluded that BP 2000 is the most promising adsorbent for the removal of carbofuran from water.

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