Adsorption of 2,4-dichlorophenoxyacetic acid using rice husk biochar, granular activated carbon, and multi-walled carbon nanotubes in a fixed bed column system

Mehdi Bahrami, Mohammad Javad Amiri and Bahareh Beigzadeh

ABSTRACT

The 2,4-dichlorophenoxyacetic acid (2,4-D) herbicide, as an aromatic hydrocarbon, is a dangerous and toxic organic pollutant among the agricultural pesticides. In this research, the performance of the biochar made from rice husk (BRH), granular activated carbon (GAC), and multi-walled carbon nanotubes (MWCNTs) was investigated for adsorption of 2,4-D in a fixed-bed column system. The influence of pH (2, 5, 7, 9), flow rate (0.5, 1, 1.5 mL min⁻¹), bed depth (3, 6, 9 cm), and influent 2,4-D concentration (50, 100, 150, 300 mg L⁻¹) on the adsorption process was evaluated. The resulting breakthrough curves indicated that the higher removal efficiency of 2,4-D took place at the lower flow rate, lower influent 2,4-D concentration, higher bed depth, and lower pH. While in most cases the removal ability of GAC was better than other adsorbents, generally, this study confirmed that the BRH, as a cheap and sustainable material, can be a viable alternative to GAC and MWCNTs for remediation and treatment scenarios, particularly in developing countries.

Key words | 2,4-D, adsorption, biochar, granular activated carbon, multi-walled carbon nanotubes

INTRODUCTION

The high consumption of pesticides and herbicides to increase agricultural production is a major environmental and health problem, in all parts of the world, and particularly in Iran. The extensive usage of herbicides by farmers has caused detected herbicide in the surface, atmosphere, and ground waters, which can have harmful effects on human health. Thus, it is important to prevent the release of these compounds into the environment due to their mobility in porous media (El Bakouri et al. 2008). 2,4-dichlorophenoxyacetic acid (2,4-D) belongs to phenoxy acetic acid, which is potentially a threat for surface and ground waters (Salman & Hameed 2010). 2,4-D is commonly used for controlling broad-leaf weeds and grass such as wheat, maize, oats, rye and cane crops due to the good selectivity and low cost (Aksu & Kabasakal 2005; Hameed et al. 2009; Salman & Hameed 2010; Deokar & Mandavgane 2015). The half-life of 2,4-D in aerobic and anaerobic aquatic environments was estimated to be 15 days and 41–335 days, respectively. The permissible limit of 2,4-D in drinking water is 100 ppb (Liang et al. 2015).

Several methods have been used to remove 2,4-D from contaminated waters, including ion-exchange (Humbert et al. 2008), advanced oxidation (Martin et al. 2008), membrane technology (Ahmad et al. 2008), biological treatment (Santacruz et al. 2005), and adsorption (Chidambaram 2016). However, among various water purification and recycling technologies, adsorption is a fast, inexpensive, and universal method. Nevertheless, the adsorption parameters acquired from batch experiments are not appropriate for most drainage water and treatment systems (Han et al. 2007; Amiri et al. 2017a, 2017b). Fixed-bed columns can be employed for treating large volumes of wastewater and determining the feasible and effective application of the adsorbents to remove the pollutants (Amiri et al. 2017a, 2017b).

In this research, the influences of granular activated carbon (GAC) and multi-walled carbon nanotubes (MWCNTs) were investigated to remove the 2,4-D pollutant from aqueous solution, also eco-friendly low-cost rice husk biochar (BRH) was examined instead of commercial adsorbents. BRH is a carbon-rich porous substance synthesized by pyrolysis of organic compounds (Kearns et al. 2014). GAC has shown great potential for elimination of different organic and inorganic pollutants (Edwin Vasu 2008) due to its properties such as microporous structure, high adsorption capacity, large surface area and high selectivity.

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Key words | 2,4-D, adsorption, biochar, granular activated carbon, multi-walled carbon nanotubes
Biochars, due to their active functional groups, high porosity, and great surface area, have been widely used to eliminate different pollutants such as organic compounds (Hallin et al. 2017), pesticides (Kearns et al. 2014), and heavy metals (Wang & Liu 2017). Nowadays, MWCNTs, as a novel adsorbent, have attracted more attention for their inimitable, layered, and hollow structures with excellent characterizations to adsorb various contaminants. These materials are favorably employed in the elimination of different pollutants such as caffeine (Bahrami et al. 2017a, 2017b), pigments (Ehyaee et al. 2017), heavy metals (Alimohammadi et al. 2017), pharmaceutical products (Zaib et al. 2016), etc.

Therefore, the main objectives of this paper were: (i) the adsorption of 2,4-D in a fixed-bed column by GAC, BRH, and MWCNTs; (ii) assessing the influence of pH, flow rate, bed depth, and influent 2,4-D concentration on the adsorption process; (iii) evaluating and comparing adsorbents to select the best adsorbent.

MATERIAL AND METHODS

Chemicals

2,4-D (purity 97.5%, 12 gr cm\(^{-3}\)) with the chemical formula \(C_8H_6Cl_2O_3\) was applied as an adsorbate without any further purification. The 2,4-D chemical structure is presented in Figure 1 (Hameed et al. 2009). 2,4-D at a concentration of 1,000 mg L\(^{-1}\) was employed as the stock solution, where the various concentrations were provided by diluting the stock solution with deionized water.

Preparation and characterization of adsorbents

Activated carbon was in granular form and MWCNTs were purchased from Merck Co. (Germany). Rice husk (RH), as one of the main agricultural wastes in Iran, was used for biochar production. The BRH was produced by the following procedure: the RH was washed with boiling distilled water and dried for 24 h at 105 \(^\circ\)C. The obtained material was crushed and passed through the various sieve sizes, until the average particle size was less than 500 \(\mu\)m. The RH powder, carbonized by purified nitrogen (99.9%) from 25 to 800 degrees Celsius with a heating rate of 10 \(^\circ\)C/min which was held at the maximum temperature for 2 h and denoted as BRH (Rostamian et al. 2014). The pore size distribution and specific surface area of the adsorbents were characterized by the Barrett-Joyner-Halenda (BJH) and Brunauer–Emmett–Teller (BET) methods, respectively (Amiri et al. 2017a), which were performed using N\(_2\) adsorption-desorption isotherms at 77 K using a Belsorp mini II instrument. The pore volume of the adsorbents was measured using N\(_2\) adsorption at a relative pressure of 0.98. Scanning electron microscopy (SEM) characterization was performed to identify the surface morphology and pore structure of adsorbents by a SEM TESCAN-Vega 3. Infrared wave numbers (cm\(^{-1}\)) of the adsorbents were recorded on KBr pellets by a JASCO FT/IR-680 plus spectrometer.

The pH drift method was employed to determine the point of zero charge (pH\(_{PZC}\)) of the BRH, GAC, and MWCNTs (Haque et al. 2014). Based on this method, 50 mL of 0.1 M KNO\(_3\) solution was transferred into a flask and the initial pH of the solution was adjusted to pH 1 to 12 using 0.1 M HNO\(_3\) and 0.1 M NaOH. Then, 50 mg of each adsorbent was added into the flask already adjusted to the desired pH and was stirred at ambient temperature for 24 h to reach the equilibrium. The final pH value of the solution was recorded at equilibrium.

Fixed-bed column experiment

A fixed bed column system was conducted in a glass column with an internal diameter of 2 cm and a height of 25 cm, to determine the dynamic behavior of 2,4-D removal by BRH, GAC, and MWCNTs. Figure 2 shows the schematic of the
experimental fixed-bed column. The experimental setup included a feed storage, Teflon tubing, a peristaltic pump, a glass column, and a sample collector. In all tests, a bulk volume of each adsorbent was packed in the column, and about 5 cm (height) of glass balls was placed at the bottom and top of the column. All tests were executed at a constant room temperature (25 ± 2 °C). The influence of pH (2, 5, 7, 9), flow rate (0.5, 1, 1.5 mL min⁻¹), bed depth (3, 6, 9 cm), and 2,4-D influent concentration (50, 100, 150, 300 mg L⁻¹) were investigated on the adsorption process by the breakthrough curves (C/C₀ changes versus time where C₀ and C indicate the influent and effluent concentration of the pollutant, respectively).

The desired values of solution pH were set out by adding 0.1 M HCl or 0.1 M NaOH and measuring with a pH meter (HACH sension3, USA). A certain discharge of 2,4-D solution was introduced to the column in the bottom-up mode and the 2,4-D breakthrough curves were obtained by measuring the concentration history of 2,4-D in the effluent by UV spectroscopy (UV/VIS 2100 S) based on absorption at 283 nm. Before measurements, 5 mL of ethyl acetate and one drop of 5 N H₂SO₄ solution were added to 5 mL of samples in a separation funnel and this mixture was shaken for 5 min and then allowed to settle for 5 min. Each experiment was conducted in triplicate and the average of the results was recorded. A standard calibration curve was provided by determining the absorbance at various 2,4-D concentrations. The value of R² is high and equal to 0.995. The calibration equation is as follows:

\[
\text{concentration} = 141.1 \times \text{ absorbance}
\]  (1)

**RESULTS AND DISCUSSION**

**Characterization of BRH, GAC, and MWCNTs**

Some of the important physical characteristics of BRH, GAC, and MWCNTs are shown in Table 1. The specific surface areas of GAC, BRH and MWCNTs were 728, 320 and 200 m² g⁻¹, respectively (see Table 1). Similarly, the pore volume of GAC, BRH and MWCNTs were 0.748, 0.431 and 0.348 cm³ g⁻¹, respectively (see Table 1), which indicate the same positive correlation between surface area and pore volume. The changes of pore structure and surface morphologies of applied adsorbents, before and after the 2,4-D adsorption, were examined by SEM. The SEM micrographs of adsorbents are shown in Figure 3. It can be seen that the carbonization heating for physical activation of RH (see Figure S1, available with the online version of this paper) caused the changing of surface precursor and the forming of different shapes and sizes of pores (see Figure 3(a)). Also, BRH and GAC have an assemblage of coarse particles of irregular shape and size with plenty of cavities and tracks (See Figure 3(a) and 3(c)) that there is a good possibility for 2,4-D to be adsorbed and trapped into the pores (Salman & Hamed 2010), due to the mesoporous structures (the pore diameter of the three adsorbents is between 2 and 50 nanometers, see Table 1). The morphology of BRH and GAC adsorbents were not obviously changed after 2,4-D adsorption (see Figure 3(b) and 3(d)), but carbon chain of MWCNTs (see Figure 3(f)) became thicker and darker than before adsorption. As revealed by the results, the surface morphology of MWCNTs was significantly changed after 2,4-D adsorption. The structure and surface functional groups of adsorbents were identified by Fourier transform infrared spectroscopy (FTIR) (Spectrum RXI). Figure 4 shows the FTIR analysis and different regions of the spectra of BRH, GAC, and MWCNTs in the range of 400–4,000 cm⁻¹, before and after the 2,4-D adsorption.

As observed in Figure 4, the FTIR spectra of the three adsorbents and their peaks before and after adsorption are very similar. The broad peak at the range of about 3,400–3,500 cm⁻¹ corresponds to hydroxyl groups (O-H) of polymeric compounds. The oxygen functional groups on the surface of the GAC, BRH and MWCNTs dramatically elevate their hydrophilic characteristics, which can play an important role for the removal of 2,4-D molecules from aqueous solution. The band in the range of 2,800–3,000 cm⁻¹ is referred to aliphatic groups (C-H). The smaller peak between 1,300–1,800 cm⁻¹ is attributed to the carbonyls group (C = O). The strong peak at 800–1,300 cm⁻¹ refers to C-O-C and C-O stretching vibration in phenols, alcohols, esters and ethers for GAC and MWCNTs (Li et al. 2018). Also, the strong peak of BRH at 1,041.37 cm⁻¹ before 2,4-D adsorption refers to silica (SiO₂).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BRH</th>
<th>GAC</th>
<th>MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>0.5–3.5 μm</td>
<td>1–1.5 mm</td>
<td>10–20 nm</td>
</tr>
<tr>
<td>Length</td>
<td>–</td>
<td>–</td>
<td>30 μm</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>18.5</td>
<td>14.6</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>SSA (m² g⁻¹)</td>
<td>320</td>
<td>728</td>
<td>200</td>
</tr>
<tr>
<td>Average pore size (nm)</td>
<td>5.9</td>
<td>4.2</td>
<td>7.2</td>
</tr>
<tr>
<td>Pore volume (cm³ g⁻¹)</td>
<td>0.431</td>
<td>0.748</td>
<td>0.348</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>1.42</td>
<td>1.58</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Figure 3 | SEM images of samples: (a) BRH, (b) BRH after 2,4-D adsorption, (c) GAC, (d) GAC after 2,4-D adsorption, (e) MWCNTs, (f) MWCNTs after 2,4-D adsorption.
The small peak between 630–720 cm\(^{-1}\) is related to the amine groups (N-H bonds). It can be observed that the FTIR results of the adsorbents were changed after adsorption, which indicates that N-H groups participate in the adsorption process. The peaks refer to alkane groups shifted to the left and emerged as new peaks, which could be attributed to change in the structure by adsorption of herbicide.

**Effect of flow rate (Q)**

The influence of the flow rate on the adsorption of 2,4-D onto the BRH, GAC, and MWCNTs was examined by changing the flow rate to 0.5, 1, and 1.5 mL min\(^{-1}\) with a constant initial concentration of 100 mg L\(^{-1}\), bed depth of 6 cm, and pH of 7. The breakthrough curves of BRH, GAC, and MWCNTs at different flow rates are presented in Figure 5. The shape of the breakthrough curves changes significantly when the adsorbent is changed, whereas the shape is very similar for different flow rates. As illustrated in Figure 5, the higher adsorption capacity of 2,4-D was observed at the lowest influent flow rate of 0.5 mL min\(^{-1}\). This can be attributed to the fact that at lower flow rates and higher breakthrough times, more adsorption sites are accessible and 2,4-D molecules adsorb easily. The breakthrough and exhaustion times moved to the origin and adsorption quantity decreased with increasing flow rate (Amiri et al. 2017a, 2017b). The higher influent flow rate creates a higher driving force for mass transport in the column and reduces the contact time; besides, there is not enough time for diffusion of 2,4-D into the adsorbent pores. Therefore, less volume of the solution is purified before leaving the column and the adsorption capacity decreases (Xu et al. 2018). In Figure 5, it can be observed that the adsorption ability of GAC is better than BRH and MWCNTs. With a flow rate of 0.5 mL min\(^{-1}\), the amounts of C/C\(_0\) for BRH, GAC, and MWCNTs achieved 0.78, 0.66, and 0.88 respectively, after six hours. However, in the short time, the adsorption ability of MWCNTs showed a better performance than the other two adsorbents. For example, after three hours with a flow rate of 0.5 mL min\(^{-1}\), the amounts of C/C\(_0\) for BRH, GAC, and MWCNTs achieved 0.45, 0.36, and 0.11 respectively. This is because, after a while, GAC and BRH presented a limited number of vacant surface adsorption sites, so they decreased or were saturated by herbicide molecules and residual sites were not easily available for 2,4-D molecules. Consequently, the adsorption of 2,4-D by GAC was higher than BRH and GAC, which might be due to the larger surface area (728 m\(^2\) g\(^{-1}\)) and adsorption pore volume (0.748 cm\(^3\) g\(^{-1}\)) of GAC. In addition, the BRH as an eco-friendly low-cost adsorbent did at least as well if
not better than the GAC adsorbent. On the other hand, the MWCNTs could potentially be employed as an efficient adsorbent to eliminate 2,4-D in a short time period.

**Effect of 2,4-D initial concentration (C₀)**

The breakthrough curves for various influent concentrations of 2,4-D (50–300 mg L⁻¹) in a fixed-bed column are shown in Figure 6, while a flow rate of 0.5 mL min⁻¹ and pH of 7 were kept constant at a bed depth of 6 cm. In the lower influent 2,4-D concentrations, the breakthrough curves shifted to the right. This is because, in the low concentration, reduction of the mass transfer driving force and diffusion coefficient led to better diffusion of 2,4-D molecules toward the adsorbent pores; consequently, the contact time increased and the solution left the column later. Hence, the adsorption ability of the adsorbents increased in lower concentrations. However, in the higher inlet concentrations, the breakthrough times moved to the origin and left. This is because, with increasing concentration,
the driving force was enhanced for diffusion of 2,4-D in the column. As well as adsorption, active sites are occupied increasingly by influent 2,4-D and the BRH, GAC, and MWCNTs active sites saturated rapidly, so that the amount of adsorption decreased (Amiri et al. 2017a, 2017b; Xu et al. 2018). After three and six hours, the amounts of C/C₀ for BRH, GAC, and MWCNTs achieved 0.34, 0.19, 0.09 and 0.67, 0.47, 0.77 respectively, while inlet concentration was 50 mg L⁻¹. As mentioned above in the flow rate section, GAC adsorbed a greater quantity of pollutant than the other two adsorbents and MWCNTs had a good performance over short periods of time, but after a while its active sites saturated very fast and the breakthrough time moved to the origin. In addition, BRH had a good performance and could compete with GAC. Similar results were reported by Xu et al. 2018.

**Effect of bed depth (H)**

Figure 7 shows the performance of breakthrough curves for 2,4-D adsorption on BRH, GAC, and MWCNTs at bed depths of 3, 6, and 9 cm with a constant flow rate of 0.5 mL min⁻¹, pH of 7, and all three adsorbents' initial concentration of 100 mg L⁻¹. As can be observed in Figure 7, the adsorption of 2,4-D by BRH, GAC, and MWCNTs was enhanced and the breakthrough times were shifted away from the origin by raising the bed depth from 3 to 9 cm. In fact, with increasing bed depth of the column, the number of vacant active sites on the adsorbents' surfaces increased and consequently the contact time between 2,4-D molecules and the adsorbents increased, which led to enhanced adsorption quantity. But at the lower column height, the vacant adsorption sites on the surfaces of the adsorbents were saturated more quickly and there was not enough time for 2,4-D molecules to diffuse in the adsorbents' pores. The breakthrough curves moved to the origin and the adsorption efficiency reduced. In addition, Figure 7 indicates that the adsorption amount at a depth of 9 cm is greater than at 3 cm. (Amiri et al. 2017a, 2017b). After 7 hours, the amounts of C/C₀ for BRH, GAC, and MWCNTs achieved 0.76, 0.61, and 0.79, respectively, while the bed depth was 9 cm.

**Effect of pH and pHₚＺＣ**

The initial pH of the solution is an important factor that influences the 2,4-D adsorption process. Initial pH affects the electrostatic interaction between 2,4-D molecules and the surface of BRH, GAC, and MWCNTs (Deokar & Mandavgane 2015). In Figure 8, the breakthrough curves of 2,4-D adsorption at pH values of 2, 5, 7, and 9 were investigated in fixed bed columns, while the initial concentration of 100 mg L⁻¹, bed depth of 6 cm, and flow rate of 0.5 mL min⁻¹ were kept constant. Results demonstrated that breakthrough times moved to the right with reducing initial pH, so that the greatest adsorption of 2,4-D was achieved at pH = 2. But at further pHs, the breakthrough curves and exhaustion time shifted to the origin. The influence of pH on the adsorption could be comprehended in terms of
pHPZC and the pKa value of 2,4-D. Surface charge of adsorbents is neutral, negative and positive, when solution pH is equal to pHPZC, over pHPZC and below pHPZC, respectively. The results showed that the pHPZC of BRH, MWCNTs, and GAC were 2, 4.1, and 8.3, demonstrating that the BRH surface was negatively charged in all studied pH greater than 2. Moreover, 2,4-D may exist as anions below pKa (2.64). Therefore, in the case of GAC and MWCNTs, the electrostatic attraction increased between positively charged adsorbents and deprotonated 2,4-D at pH = 2. In the case of BRH, electrostatic repulsion might occur between negatively charged BRH and the 2,4-D molecule at pH > 2. Although, the slight shift in the spectrum of the BRH after 2,4-D adsorption demonstrates the interaction between it and 2,4-D is based on hydrogen bonds. Also, with increasing pH, more oxygen-containing groups are built on the surface of the BRH, GAC, and MWCNTs so that they lead to lower availability of the active and vacant pores on the surface of the adsorbents to adsorb 2,4-D molecules, hence the adsorption efficiency is reduced.

Kinetic studies

Kinetic studies of 2,4-D were performed by adding 0.1 g of GAC, BRH and MWCNTs to 100 mL of 50 mg L⁻¹ 2,4-D solution at pH = 2. The samples were shaken and filtered at various time intervals (1, 5, 20, 40, 60, 80, 100, 120 min). The kinetic data were fitted to the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models and the results are presented in Table 2. The details of the models were presented by Gil et al. (2018) and are presented in Table S1 (available with the online version of this paper). From Table 2, the pseudo-second-order model provides the best performance and the correlation coefficients (R²) are higher than 0.98 for the three adsorbents. The experimental adsorption capacities for GAC, BRH and MWCNTs were 27.1, 24.63 and 21.87 mg g⁻¹, respectively.

Table 2 | Kinetic parameters for the adsorption of 2,4-D

<table>
<thead>
<tr>
<th>Model</th>
<th>Adsorbents</th>
<th>GAC</th>
<th>BRH</th>
<th>MWCNTs</th>
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<tr>
<td>Second-order model</td>
<td></td>
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<tr>
<td>k₂ (g (mg min⁻¹))</td>
<td></td>
<td>0.0031</td>
<td>0.0013</td>
<td>0.156</td>
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<tr>
<td>q₂ (mg g⁻¹)</td>
<td></td>
<td>28.67</td>
<td>27.16</td>
<td>21.88</td>
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<tr>
<td>R²</td>
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<td>0.986</td>
<td>0.987</td>
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<td>First-order model</td>
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<td>k₁ (min⁻¹)</td>
<td></td>
<td>3.12</td>
<td>6.56</td>
<td>0.371</td>
</tr>
<tr>
<td>q₁ (mg g⁻¹)</td>
<td></td>
<td>22.77</td>
<td>18.25</td>
<td>22.07</td>
</tr>
<tr>
<td>R²</td>
<td></td>
<td>0.936</td>
<td>0.967</td>
<td>0.971</td>
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<tr>
<td>Inter-particle model</td>
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<tr>
<td>kₓ (mg (g min⁻¹/²)⁻¹)</td>
<td></td>
<td>2.27</td>
<td>2.4</td>
<td>0.358</td>
</tr>
<tr>
<td>R²</td>
<td></td>
<td>0.936</td>
<td>0.976</td>
<td>0.407</td>
</tr>
</tbody>
</table>
respectively. The results revealed that the calculated adsorption capacities are close to the experimental data. The greatest second-order rate constant was observed for MWCNTs (0.156 g mg\(^{-1}\)min\(^{-1}\)), which indicates MWCNTs reacted with the 2,4-D molecule much faster than the two other adsorbents.

**Mathematical models**

The dynamic adsorption of 2,4-D with the GAC, BRH and MWCNTs was examined using two mathematical models including the Thomas (Thomas 1944) and Yan (Yan et al. 2001) models. These equations, in non-linear forms and associated parameters, are presented in the supplementary data. The experimental data were fitted to models using non-linear regression analysis. The accuracy of the Thomas and Yan models was evaluated based on the calculated determination coefficient (R\(^2\)). The results showed that the experimental data were satisfactorily described by the Thomas and Yan models. Although the Yan model was able to fit well the breakthrough curves acquired at each operating condition, an approximately perfect match between the experimental data and the estimated ones was achieved using the Thomas model (higher R\(^2\)). The Thomas constants (k\(_T\) and q\(_T\)), as well as the Yan parameters (k\(_Y\) and q\(_Y\)), for describing dynamic adsorption of 2,4-D under various operational parameters for GAC, BRH and MWCNTs are presented in Tables S2, S3 and S4, respectively (available with the online version of this paper). The q\(_T\) for GAC, BRH and MWCNTs was found to be between 85.29 and 294 mg g\(^{-1}\) (see Table S2), 78.32 and 252.34 mg g\(^{-1}\) (see Table S3) and 53.21 and 208.19 mg g\(^{-1}\) (see Table S4), respectively, which confirm the results from the experimental data. Also, the q\(_Y\) values were found to be in the range of 27.18 to 68.31 mg g\(^{-1}\) for GAC, 24.18 to 53.17 mg g\(^{-1}\) for BRH and 7.86 to 43.79 mg g\(^{-1}\) for MWCNTs. The k\(_T\) for GAC, BRH and MWCNTs was found to be between 0.0018 and 0.0098 mL min\(^{-1}\) mg\(^{-1}\) (see Table S2), 0.0014 and 0.0094 mL min\(^{-1}\) mg\(^{-1}\) (see Table S3) and 0.018 and 0.087 mL min\(^{-1}\) mg\(^{-1}\) (see Table S4), respectively.

**CONCLUSIONS**

In this study, the adsorption ability of BRH, GAC, and MWCNTs was investigated for removal of 2,4-D in a fixed-bed column system. In this regard, the influence of parameters such as pH, Q, H, and C\(_0\) on the adsorption process was evaluated. The results demonstrated that the GAC had a better adsorption ability than the other two adsorbents. Nevertheless, it is not economical for treatment of large volumes of wastewater, thus BRH, as a cheap and sustainable material, can be a viable alternative to GAC and MWCNTs for remediation and treatment scenarios, particularly in developing countries. Also, MWCNTs have not been used for purification at large scales yet. However, MWCNTs can be an excellent choice for removal of herbicides if the treatment equilibrium time is an important choice, because they can remove acceptable amount of pollutants in a short time.

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