2,4-dichlorophenoxyacetic acid adsorption from contaminated water through activated carbon reclaimed with zero-valent iron and titanium dioxide

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Activated carbon;
Zero-valent iron;
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Abstract. The sol-gel method was used for the synthesis of zero-valent iron/titanium dioxide supported on activated carbon (Fe⁰/TiO₂/AC) adsorbents, and the adsorbents were comprehensively characterized by XRF, XRD, FT-IR, BET, FE-SEM, and EDX analyses. The batch experiments were performed to evaluate the effect of adsorbent type, pH of solution, pollutant initial concentration, and contact time on the 2,4-dichlorophenoxyacetic acid (2,4-D) adsorption efficiency. The equilibrium experiments revealed that the Langmuir isotherm was in good agreement with the adsorption equilibrium data, whereas the adsorption kinetic experiments indicated that the adsorption procedure was described perfectly through a pseudo-first-order kinetic model. The obtained maximum adsorption capacities from Langmuir isotherms of 86.5, 87.5, 86.57, and 88.76 mg/g were achieved for Activated Carbon (AC), zero-valent iron/activated carbon (Fe⁰/AC), titanium dioxide/activated carbon (TiO₂/AC), and Fe⁰/TiO₂/AC at the 2,4-D initial concentration of 90 mg/L, pH = 4 and 25°C, respectively.

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1. Introduction

Improving the quality of agricultural products and pest control has been the main application of pesticide consumption in recent years [1,2]. 2,4-dichlorophenoxyacetic acid (2,4-D) is a current herbicide, due to its high selectivity and economy [3], which controls broad leaf weeds [1,4-6]. The maximum allowable amount of 2,4-D is 0.03 mg/L in an aqueous medium [9]. The main features of 2,4-D include relative toxicity with high movability and durability in an aqueous medium [10]. Other properties of 2,4-D include being non-volatile and highly soluble in water [7]. The half-life of 2,4-D is within 6-170 days in an aqueous medium [11]; thus, removing this herbicide from contaminated water depends on the quantitative and qualitative acceptors of water resource. Contamination of surface water and groundwater by 2,4-D can lead to serious threats, such as cancer and reproductive problem, to human health [6]; therefore, it is necessary to remove this contaminant from water sources.

Adsorption, nanofiltration, electrocoagulation, photocatalytic degradation, photo-fenton, ultrasound, biological processes, and sedimentation are the common methods for treatment of the contaminated water containing pesticides [1,2]. The removal of pesticides by chemical coagulation, photo oxidation, sedimentation, filtration, and adsorption depends on the chemical nature of pesticide and the mechanism of the process [12]. Utilization of different methods, such as
adsorption, nanofiltration, advanced oxidation process, photo-catalytic degradation, photo-Fenton, biological oxidation, and aerobic degradation has been introduced for 2,4-D elimination [3].

The removal of pesticides from an aquatic environment has been carried out by different adsorbents and photocatalysts. Recently, nanocomposites and bio nanocomposites have been used to remove pesticides [13]. Different adsorbents have been used to remove pesticides in previous studies including rice husk [14,15], Activated Carbon (AC) [16-18], zeolites [19,20], montmorillonite and bentonite [21], and calcite and kaolinite [22]. In addition, biopolymers, such as chitosan [23,24] and alginate [24], have been used for the pesticides adsorption. Porous structure, economy, accessibility, and mechanical strength are the promising features of an AC adsorbent [25]. In recent researches, several adsorbents have been applied to adsorption of 2,4-D that include activated carbon-based data palm pits [1], activated carbon from wood composite [2], adsorbents prepared from groundnut shell (GSA, GSC, and GSAC) [3], single-walled carbon nanotube [4], MIEX resin [5], activated carbon fiber modified by nitric acid [6]. Langsat Empty Fruit Bunch Activated Carbon (LEFBAC) [7], pumpkin seed hull activated carbon [10], rice husk ash [15], granular activated carbon [26], modified granular activated carbon [27], activated carbon from date stones (DSAC) [28], Coconut Activated Carbon (CAC) [29], Cornco Activated Carbon (CCAC) [30], Coconut Shell Activated Carbon (CSAC) [31], activated carbon prepared from barhi date seeds (BDSAC) [32], Granular Activated Carbon Filtersorb 300 (GAC-F300) [33], and graphite carbon nanostructures prepared from biomass [34].

Nanoparticles have a significant degradation performance because of their great surface area and favorable adsorption capacity [35]. The superior reactivity of Zero-Valent Iron (ZVI) nanoparticles is because of the high specific surface area [36]. Because of the high surface energy and natural magnetic interaction, this nanoparticle has a high inclination for cumulation. The aggregation of nanoparticles reduces the surface area, mobility, and activity [37]. As ZVI is exposed to air, it is oxidized which loses its high activity [38]. In order to prevent the aggregation, the nanoparticles are impregnated into a base substance like AC [25,39-41], graphite [42], silica [43,44], bentonite [45], or a membrane [46,47].

Titanium dioxide nanoparticles have high oxidation capability and are non-toxic, cheap and lightly stable [48]. However, their application in a treatment process is limited due to the low adsorption capacity [49]. BET analysis showed that titanium dioxide powder with anatase and rutile phases had specific surface area of about 67 m²/g [50]. Materials such as biopolymer nanofibers [51], cotton fiber [52], Al₂O₃ [53], SiO₂ [54], and AC [49,55-60] are applied as the support for titanium dioxide nanoparticle. It has been reported that using silica, glass, polystyrene spheres, and AC as supports for TiO₂ led to higher photocatalytic activity and surface area [61].

Applying adsorption as a treatment process will cause secondary pollution that is unfavorable. In contrary, AOP enjoys several advantages: rapid reaction rate, lack of sludge production, and high potential for toxicity reduction. However, AOP is much more complex than the adsorption and needs major investments, which can be counted as disadvantageous. To the best of our knowledge, the performance of Fe⁰/TiO₂/AC for 2,4-D adsorption has not been studied in previous studies. The main approach to future researches includes adopting simultaneous adsorption and AOP together. The synergistic effect between adsorption and AOP is an important issue as the impregnation of the AC with nanoparticles may result in pore collapse and lose active sites for adsorption. The present study investigates the effect of AC impregnation with nanoparticles on the adsorption capacity of 2,4-D from an aqueous medium without light illumination.

In this research, the reduction liquid phase method was applied to Fe⁰/AC adsorbent synthesis and the sol-gel technique was used for TiO₂/AC, ZVI/TiO₂ based on the AC (Fe⁰/TiO₂/AC) adsorbents. The adsorbents were specified comprehensively by XRF, XRD, FT-IR, FE-SEM, EDX, and BET analyses. The adsorption process and adsorption capacity of (2,4-D) of the adsorbents were evaluated by kinetics and adsorption equilibrium studies in a series of batch experiments.

2. Materials and methods

2.1. Adsorbate

2.4-D with 97% purity was prepared from Sigma-Aldrich and applied as the adsorbate. The molecular weight and maximum UV absorption of 2,4-D are 221.04 g/mol and 284 nm. In addition, 2,4-D solubility in water is 900 mg/L at 293 K [2]. The standard stock solution was prepared by dissolving a sufficient amount of 2,4-D in distilled water. All other chemicals were of analytical grade and applied without any further purification.

2.2. Adsorbents preparation

The precursors of titanium dioxide and ZVI include titanium tetrachloride (TiCl₄) and iron (II) sulfate hydrate (FeSO₄·7H₂O), respectively. The sol-gel method was adopted for synthesizing the Fe⁰/TiO₂/AC adsorbent. Firstly, a solution consisting of 72 ml of ethanol and 18 ml of deionized water (ethanol/deionized water: 4/1 v/v) was prepared in a three-neck flask, and 7 ml of TiCl₄ was mixed with 36 ml of deionized water.
The TiCl₄ solution was added slowly into the three-neck flask. 0.25 g of FeSO₄·7H₂O was poured, and then the flask was placed in an ultrasonic water bath for 20 min. Afterwards, the solution was mixed by a magnetic stirrer for 30 min. 50 ml of 1 M solution of sodium borohydride (NaBH₄) was gradually added drop-wise to the prepared solution at 5-7 ml/min rate. Likewise, the solution was mixed well using a magnetic stirrer for 30 min. Consequently, 495 g of AC was poured gradually into the solution, and the mixture was agitated for 1 h. The final solution was placed at ambient temperature for 24 h. Then, the solution was filtered and washed with ethanol in two stages and placed in an oven at 120°C for 2 h. The calculation process was performed to complete the synthesis process in a furnace at 400°C for 2 h. Finally, the synthesized adsorbent was poured into a black bottle and kept there at 15-20°C until use. The mass ratio of Fe³⁺ to TiO₂ was 1%. Adsorbents Fe³⁺/AC and TiO₂/AC were synthesized similarly according to the above-mentioned procedure.

2.3. Characterization of adsorbents

X-Ray Fluorescence (XRF) analysis (Bruker, Model S4 Pioneer, Germany) was performed to specify the adsorbents composition. X-Ray Diffraction (XRD) was accomplished with a XRD diffractometer (Bruker, Model D8 Advance, Germany) within the scanning range of 2θ = 10°-80°. For the analysis of XRD peaks, the X’Pert HighScore software was used. The point of zero charge (pHₚzc) of the adsorbent was measured according to the procedure described by Reddy et al. (2010) [62]. Fourier transform infrared (FTIR) spectroscopy analysis was carried out by a FTIR spectrometer (Jasco, Model 6300, Japan) within a scanning range of 400-4000 cm⁻¹ to determine the surface functional groups and surface chemical characteristics of the adsorbent. The surface physical properties were identified by a Brumauer-Emmett-Teller (BET) (Microtrac Bel Corp, Model Belsorp mini, Japan) analysis. The Nitrogen adsorption was used to specify surface area and porosity attributes at 77 K. The surface morphology of adsorbents and their particle size distributions were characterized by Field Emission Scanning Electron Microscopy (FE-SEM) (Zeiss, Model Sigma-VP 500, Germany) analysis. Elemental analysis was performed using Energy Dispersive X-ray (EDX) (Oxford Instrument, England).

2.4. Batch adsorption studies

The batch experiments were accomplished in 50-ml Erlenmeyer flasks containing 0.02 g of adsorbent and 20 ml of 2,4-D solution with different initial concentrations (15-90 mg/L) and pHs (4, 7, and 10). The flasks were agitated for 6 to 8 h in a shaking incubator (N-Biotek, Model NB-205v, South Korea) at 130 rpm and 25°C. After adsorption contact, the sample was centrifuged (Hanil, Model supra 22-k, South Korea) at 15000 rpm for 10 min. The 2,4-D concentration was analyzed by an UV-Vis spectrophotometer (Jasco, Model V-570, Japan) at the wavelength of 283 nm. The pH of solution was adjusted through adding 1 M sodium hydroxide and 0.1 M sulfuric acid and measured by a pH meter (Elmetron, Model CP-505, Poland).

The adsorbed 2,4-D capacity at time t, qₜ (mg of adsorbate/g of adsorbent) and the removal efficiency of 2,4-D, E(%) were calculated through Eqs. (1) and (2), respectively:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  
\[ E\% = \frac{C_0 - C_t}{C_0} \times 100 \]  

where \( C_0 \) (mg/L) and \( C_t \) (mg/L) are the initial concentration and concentration at time t, respectively. V (L) is the solution volume, and m (g) is the adsorbent mass. The adsorption equilibrium capacity, \( q_e \) (mg of adsorbate/g of adsorbent), is determined by Eq. (3):

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

where \( C_e \) (mg/L) is the 2,4-D equilibrium concentration.

For AC, Fe³⁺/AC, and TiO₂/AC adsorbents, the equilibrium was achieved after 4 h, while, in the case of Fe³⁺/TiO₂/AC, it was 6 h. To ensure the equilibrium condition, the adsorption experiments were performed within 6 to 8 h.

3. Results and discussion

3.1. Adsorbents characterization

The results of XRF analysis are shown in Table 1. The results show that the weight percentages of Fe³⁺, TiO₂, and the total Fe³⁺ and TiO₂ are almost identical in the Fe³⁺/AC, TiO₂/AC, and Fe³⁺/TiO₂/AC adsorbents, respectively. In addition, the weight ratio of Fe³⁺ to TiO₂ in Fe³⁺/TiO₂/AC adsorbent is close to 1%.

The XRD patterns of AC, Fe³⁺/AC, TiO₂/AC, and Fe³⁺/TiO₂/AC adsorbents are illustrated in Figure 1. The XRD of AC (Figure 1(a)) shows a peak at about 24.4° (002) which corresponds to the reflection of aromatic layers in carbon on the (002) plane. This peak indicates an amorphous structure present in the AC adsorbent. The corresponding peaks occur at 26.4°, 23.47°, and 23.45° for Fe³⁺/AC (Figure 1(b)), TiO₂/AC (Figure 1(c)), and Fe³⁺/TiO₂/AC (Figure 1(d)), respectively.

An obvious peak of Fe³⁺ is observed at 44.7°(110) and 44.05° in Fe³⁺/AC and Fe³⁺/TiO₂/AC adsorbents,
Table 1. XRF analysis of Fe\(^{0}\)/AC, TiO\(_2\)/AC, and Fe\(^{0}\)/TiO\(_2\)/AC nanocomposites (weight%).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe(^{0})/AC</th>
<th>TiO(_2)/AC</th>
<th>Fe(^{0})/TiO(_2)/AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>-</td>
<td>14.75</td>
<td>15.11</td>
</tr>
<tr>
<td>Fe(_{2})O(_3)</td>
<td>20.83</td>
<td>0.03</td>
<td>0.238</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>4.82</td>
<td>-</td>
<td>0.164</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>3.72</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.27</td>
<td>1.31</td>
<td>1.37</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>0.17</td>
<td>0.201</td>
<td>0.13</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.14</td>
<td>0.138</td>
<td>0.096</td>
</tr>
<tr>
<td>CaO</td>
<td>0.12</td>
<td>0.22</td>
<td>0.103</td>
</tr>
<tr>
<td>Cl</td>
<td>0.034</td>
<td>3.06</td>
<td>1.91</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.025</td>
<td>0.107</td>
<td>0.028</td>
</tr>
<tr>
<td>MnO</td>
<td>0.024</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuO</td>
<td>0.011</td>
<td>0.001</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LOI</td>
<td>69.75</td>
<td>80.03</td>
<td>80.62</td>
</tr>
<tr>
<td>Total</td>
<td>99.92</td>
<td>99.96</td>
<td>99.93</td>
</tr>
</tbody>
</table>

Figure 1. XRD Patterns of (a) AC, (b) Fe\(^{0}\)/AC, (c) TiO\(_2\)/AC, and (d) Fe\(^{0}\)/TiO\(_2\)/AC.

respectively, indicating the low oxidation level. The peak of Fe\(^{0}\) shows good crystallinity of Fe\(^{0}\).

The six diffraction peaks of anatase TiO\(_2\) are observed clearly at 25.9° (101), 38.4° (004), 48.1° (200), 54.1° (105), 54.8° (211), and 62.8° (204) for TiO\(_2\)/AC. In addition, for TiO\(_2\)/AC adsorbent, the rutile peaks of TiO\(_2\) occur at 27.25° (110), 36.5° (101), 40.97° (111), and 54.3° (211).

Similarly, the peaks of anatase TiO\(_2\) for Fe\(^{0}\)/TiO\(_2\)/AC are observed at 25.6°, 37.9°, 48.36°, 53.96°, 55.03°, 63.2°, 69.2°, and 70.9°. The two peaks of rutile TiO\(_2\) are observed at 36.3° and 40.92°. The XRD patterns of TiO\(_2\)/AC and Fe\(^{0}\)/TiO\(_2\)/AC reveal the formation of mixed phases in the adsorbents.

The FT-IR spectroscopy explains the presence of functional groups on the adsorbents surface. The FT-IR spectra of AC, Fe\(^{0}\)/AC, TiO\(_2\)/AC, and Fe\(^{0}\)/TiO\(_2\)/AC are shown in Figure 2. The FT-IR spectrum of AC (Figure 2(a)) has a broad peak at 3436.5 cm\(^{-1}\), which is attributed to the –OH stretch vibration of a hydroxyl group. The absorbance peak at 1703.8 cm\(^{-1}\) shows the C=O stretching vibration of carbonyl and carboxyl groups. The band at 1564 cm\(^{-1}\) is related to the C=C stretching of the aromatic group. The peak at 1430.9 cm\(^{-1}\) corresponds to the –C-H bending vibration of the alkane group. The absorbance peaks at 1117.6 and 1006.4 cm\(^{-1}\) describe the C-O stretch vibrations and show the presence of the hydroxyl, ether and ester functional groups. The bands at 799.3 and 876.5 cm\(^{-1}\) are relevant to the C-CI stretching vibration of alkyl halide. The final peak at 610.4 cm\(^{-1}\) is attributed to the C-CI stretching vibration of alkyl halide. In the FT-IR spectrum of Fe\(^{0}\)/AC (Figure 2(b)), five different peaks' intensities exist at 465.7 cm\(^{-1}\), 615.2 cm\(^{-1}\), 1122.7 cm\(^{-1}\), 1565 cm\(^{-1}\), and 3423 cm\(^{-1}\) that illustrate the hematite (α-Fe\(_{2}\)O\(_3\)) [63], maghemite (γ-Fe\(_{2}\)O\(_3\)) [63], γ-FeOOH-lepidocrocite [63], C≡C stretch vibration [64], and O-H stretching vibration of hydroxyl group. 1152.2 cm\(^{-1}\), 1571.7 cm\(^{-1}\), 1720.2 cm\(^{-1}\), and 3428 cm\(^{-1}\) of FT-IR spectrum of TiO\(_2\)/AC (Figure 2(c)) exhibit Ti-O functional group of TiO\(_2\) nanoparticles [65], C≡C stretch vibration [64], C=O stretch vibration [64], and O-H stretching vibration of a hydroxyl group. In the spectrum of Fe\(^{0}\)/TiO\(_2\)/AC nanocomposite (Figure 2(d)), five different peaks' intensities are observed at 669.2 cm\(^{-1}\), 1136.8 cm\(^{-1}\), 1576.5 cm\(^{-1}\), 1720.2 cm\(^{-1}\), and 3391.2 cm\(^{-1}\) that indicate the symmetric Fe-O stretch [63], Ti-O functional group of TiO\(_2\) nanoparticles [65], C≡C stretch vibration [64], C=O stretch vibration [64], and O-H stretching vibration of H\(_2\)O [63], respectively.

The BET surface area, Langmuir surface area, total pore volume, and average pore diameter are achieved through the nitrogen adsorption-desorption. Figure 3 indicates the nitrogen adsorption and desorption for AC (Figure 3(a)), Fe\(^{0}\)/AC (Figure 3(b)), TiO\(_2\)/AC (Figure 3(c)), and Fe\(^{0}\)/TiO\(_2\)/AC (Figure 3(d)) at 77 K. The obtained isotherms have a typical type IV with a H3 hysteresis loop. The isotherms of AC, Fe\(^{0}\)/AC, TiO\(_2\)/AC, and Fe\(^{0}\)/TiO\(_2\)/AC adsorbents indicate a remarkable improvement of relative pressure at the P/P\(_0\) less than 0.1 to about 0.2, exhibiting that all adsorbents are microporous. In addition, the mesoporous structures' presence is identified with respect to the closure of hysteresis loops at relative pressure rates of P/P\(_0\) = 0.3026 (AC), P/P\(_0\) = 0.2982 (Fe\(^{0}\)/AC), P/P\(_0\) = 0.3003 (TiO\(_2\)/AC), and P/P\(_0\) = 0.3908 (Fe\(^{0}\)/TiO\(_2\)/AC).

Table 2 indicates the surface and pore properties of the adsorbents. The specific surface areas of Fe\(^{0}\)/AC, TiO\(_2\)/AC, and Fe\(^{0}\)/TiO\(_2\)/AC adsorbents decrease compared to that for the AC, which may be due to the occupation of the AC surface with Fe\(^{0}\) and TiO\(_2\) nanoparticles. Accordingly, the porosity decreases due
Figure 2. FT-IR spectra of: (a) AC, (b) Fe\(^0\)/AC, (c) TiO\(_2\)/AC, and (d) Fe\(^0\)/TiO\(_2\)/AC.

Figure 3. Nitrogen adsorption-desorption isotherms and surface characteristics of: (a) AC, (b) Fe\(^0\)/AC, (c) TiO\(_2\)/AC, and (d) Fe\(^0\)/TiO\(_2\)/AC.

to pore collapse caused by the impregnation of AC with nanoparticles.

The morphological structures of AC, Fe\(^0\)/AC, TiO\(_2\)/AC, and Fe\(^0\)/TiO\(_2\)/AC adsorbents were analyzed by FE-SEM micrograph. As shown in Figure 4, the AC support indicates a uniform morphology and slit-shaped pores. The surface of Fe\(^0\)/AC showed a few agglomerations in some local areas (Figure 4(b)). A comparison of the AC and the synthesized adsorbents' morphological structure indicates the presence of a new
**Table 2.** Surface characteristic of AC, Fe$^0$/AC, TiO$_2$/AC, and Fe$^0$/TiO$_2$/AC adsorbents.

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>AC</th>
<th>Fe$^0$/AC</th>
<th>TiO$_2$/AC</th>
<th>Fe$^0$/TiO$_2$/AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>447.66</td>
<td>361.56</td>
<td>447.16</td>
<td>402.13</td>
</tr>
<tr>
<td>Langmuir surface area (m$^2$/g)</td>
<td>481.38</td>
<td>414.91</td>
<td>569.73</td>
<td>420.51</td>
</tr>
<tr>
<td>External surface area (m$^2$/g)</td>
<td>78.43</td>
<td>49.58</td>
<td>50.83</td>
<td>66.82</td>
</tr>
<tr>
<td>Micropore surface area (m$^2$/g)</td>
<td>369.23</td>
<td>314.98</td>
<td>396.33</td>
<td>335.31</td>
</tr>
<tr>
<td>Total pore volume (cm$^3$/g)</td>
<td>0.53</td>
<td>0.403</td>
<td>0.479</td>
<td>0.496</td>
</tr>
<tr>
<td>Micropore volume (cm$^3$/g)</td>
<td>0.352</td>
<td>0.273</td>
<td>0.368</td>
<td>0.322</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>4.739</td>
<td>4.422</td>
<td>4.284</td>
<td>4.937</td>
</tr>
</tbody>
</table>

**Figure 4.** FE-SEM micrograph of: (a) AC, (b) Fe$^0$/AC, (c) TiO$_2$/AC, and (d) Fe$^0$/TiO$_2$/AC.

structure due to the impregnation process. The FE-SEM micrograph shows mesoporous and microporous surfaces of AC, whereas the nanoparticles are deposited onto the external surface.

The EDX spectrum of adsorbents is shown in Figure 5. The EDX spectrum of AC (Figure 5(a)) indicates that carbon is the main element. Similarly, the EDX spectrum of Fe$^0$/AC (Figure 5(b)), TiO$_2$/AC (Figure 5(c)), and Fe$^0$/TiO$_2$/AC (Figure 5(d)) adsorbents indicates the presence of C, Fe, C:Ti:O and C:Fe:Ti:O as the main elements, confirming the successful synthesis of the adsorbents.

### 3.2. Effect of solution pH on the 2,4-D adsorption

In an adsorption process mechanism, adsorption medium pH displays a significant role in a pollution treatment [2]. The electrostatic interactions between adsorbent and adsorbate are controlled with pH [66]. The characteristics, such as the adsorbent surface charge, ionization degree, and speciation of adsorbate, are dependent on pH solution [26]. The 2,4-D dissociation constant is 2.73 at 25°C [4].

The protonated and deprotonated species exist when the solution pH is below 2 and above 4.5, respectively [67]. Therefore, at higher pH, the 2,4-D is separated and their higher ratio exists in the anion form in the water solution. The effect of solution pH on the removal efficiency of 2,4-D adsorption equilibrium capacity ($q_e$) of 2,4-D by adsorbents was investigated at 4.7,10 the pH values, with the initial concentration of 90 mg/L at 25°C. The pHpzc is measured 6.6, 6.8, 6.2, and 6.35 for AC, Fe$^0$/AC, TiO$_2$/AC, and Fe$^0$/TiO$_2$/AC adsorbents, respectively.
The results indicate that, by an increment in the solution pH from 4 to 10, the adsorption equilibrium capacity and the removal efficiency of 2,4-D decrease for all the adsorbents. The surface charge of 2,4-D is always negative in the pH range (pH > P<sub>k<sub>a</sub>); however, the surface charge of adsorbents depends on the relation between pK<sub>zc</sub> and solution pH. The surface charge of adsorbents is positive when pH < pK<sub>zc</sub>, and this is negative when pH > pK<sub>zc</sub>. As a result, an increase in the pH value can lead to an increase in the electrostatic interaction between the adsorbents’ surface and 2,4-D molecules. In addition, the dissociation degree of 2,4-D is increased by the enhancement solution pH, and then the anion species of 2,4-D are predominant in the aqueous solution. The adsorption equilibrium capacities of AC, Fe<sup>0</sup>/AC, TiO<sub>2</sub>/AC, and Fe<sup>0</sup>/TiO<sub>2</sub>/AC adsorbents decrease from 70.7 to 67.8, 73.6 to 69.5, 73.4 to 68.4, and 75.8 to 71.5 mg of adsorbate/g of the adsorbent, respectively, due to an increase in the solution pH from 4 to 10 at the initial concentration of 90 mg/L. In a similar condition, the removal efficiency of 2,4-D decreases from 78.5% to 75.3%, 81.8% to 77.2%, 81.5% to 75.9%, and 84.1% to 79.4%, respectively.

### 3.3. Effect of pollutant initial concentration and contact time on the 2,4-D adsorption

Figure 6 demonstrates the effect of the 2,4-D initial concentration at 15, 30, 45, 60, 75, and 90 mg/L with solution pH of 4 at 25°C. The adsorption equilibrium capacities of AC, Fe<sup>0</sup>/AC, TiO<sub>2</sub>/AC, and Fe<sup>0</sup>/TiO<sub>2</sub>/AC adsorbents increase from 14.3 to 70.7, 14.4 to 73.6, 14.3 to 73.4, and 14.5 to 75.8 mg of adsorbate/g of the adsorbent by increasing the 2,4-D initial concentration within 15-90 mg/L, respectively, because the driving force (concentration gradient) is enhanced at the higher initial concentrations. In addition, the collision between 2,4-D molecules and surface adsorbent is increased. The removal efficiencies of 2,4-D for AC, Fe<sup>0</sup>/AC, TiO<sub>2</sub>/AC, and Fe<sup>0</sup>/TiO<sub>2</sub>/AC adsorbents are decreased from 95.3% to 78.5%. 96% to 81.8%, 95.5% to 81.5%, and 96.8% to 84.2%, respectively, while the initial concentration changes from 15 to 90 mg/L at pH = 4. Furthermore, since the adsorption process is faster at the smaller concentration of adsorbate, the rate of adsorption is decreased by increasing 2,4-D initial concentration.

Figure 6 indicates the influence of contact time on the removal efficiency at different 2,4-D initial concentrations and pH = 4. The adsorption rate increased quickly with contact time at the initial times and, then, decreased gradually until equilibrium was achieved after 6-8 hours for all the initial concentrations and adsorbents at pH = 4. The observed faster rate at the initial times could be due to the presence and availability of unoccupied active sites on the surface of adsorbents. However, the active sites are occupied gradually, and the adsorption rate is decreased.

### 3.4. Effect of adsorbent type on the 2,4-D adsorption

The presence of the functional groups, solubility in water, polarity, ionic nature, bonding mechanism properties are the impressive parameters of the adsorption efficiency depending on the surface chemistry and adsorbate chemical properties [68]. The removal efficiencies of AC, Fe<sup>0</sup>/AC, TiO<sub>2</sub>/AC, and Fe<sup>0</sup>/TiO<sub>2</sub>/AC...
adsorbents are 78.5%, 81.8%, 81.5%, and 84.2%, respectively, at the initial concentration of 2.4-D 90 mg/L and pH = 4. Although the specific surface areas of the synthesized adsorbents are less than that of the AC, the removal efficiency of 2,4-D by the synthesized adsorbents is higher than that by the AC. It is explained that a combined contaminant removal by a reduction reaction on the surface of ZVI reductant and physical adsorption co-precipitation processes may occur. The contaminant is adsorbed either on ZVI and AC surfaces or is co-precipitated on the formed iron oxide/oxyhydroxide surface in ZVI/H2O system [69]. The contaminant may be also degraded by the reactive oxygen species, produced through reaction of ZVI with the dissolved oxygen molecules [70]. The interaction between TiO2 and oxygen molecules or water molecules may also lead to the production of oxidative agents; hence, the 2,4-D concentration in solution is reduced [71].

3.5. Adsorption kinetics

The kinetic data fit the nonlinear form of pseudo-first-order and pseudo-second-order kinetic models using the curve fitting toolbox of Matlab software 2013, as shown in Figure 7.

The Lagergren pseudo-first-order model [72] is expressed by Eq. (4):

\[ q_t = q_e \left(1 - e^{-k_1 t}\right), \]  

where \( k_1 \) (1/min), \( q_e \) (mg/g), and \( t \) (min) are the pseudo-first-order kinetic rate constant, adsorption equilibrium capacity, and contact time, respectively.

The pseudo-second-order model [73] is represented by Eq. (5):

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \]  

where \( k_2 \) (g/mg min) is the pseudo-second-order rate constant.

The correlation coefficient \((R^2)\) and Root-Mean-Square Error (RMSE) are computed to evaluate the fitting goodness. The RMSE is used to determine the most appropriately practical model. The obtained kinetic parameters for the pseudo-first-order and pseudo-second-order kinetic models are summarized in Table 3.

The adsorption of 2,4-D onto all adsorbents is best explained by the pseudo-first-order kinetic model. The result demonstrates that the adsorption is more inclined towards physisorption.

The Weber-Morris model (intraparticle diffusion) [74] is applied to define the adsorption mechanism. It is expressed by Eq. (6):

\[ q_t = k_d t^{0.5} + C_i, \]  

Figure 6. Effect of initial concentration and contact time of 2,4-D on the removal efficiency. (a) AC, (b) Fe0/AC, (c) TiO2/AC, and (d) Fe0/TiO2/AC (pH = 4, adsorbent = 1 g/L, \( T = 25^\circ \text{C}, \) agitation speed = 130 rpm).
where \( k_1 \) (mg/g min\(^{0.5}\)) and \( C_i \) are the intraparticle diffusion rate constant and the thickness of boundary layer, respectively.

There are three forms for the regression of \( q_t = f(t) \) (\(^{0.5}\)). The intraparticle diffusion is the dominant mechanism of the adsorption procedure, when the regression is linear and intercept is equal to zero (\( C_i = 0 \)). The intraparticle diffusion participates in adsorption mechanism, but not as the limiting step, when the regression is linear and intercept is equal to zero (\( C_i \neq 0 \)). The multi-linear plot illustrates that the adsorption mechanism incorporates different steps. The initial and second sections of the diagram represent external adsorption and intraparticle diffusion, respectively [26]. In this study, the regression is linear and intercept is not equal to zero (\( C_i \neq 0 \)); therefore, the intraparticle diffusion participates in adsorption mechanism, but not as the limiting step (Figure 8).

3.6. Adsorptions isotherms
The adsorption equilibrium data are in agreement with the nonlinear form of Langmuir, Freundlich, Templkin, and Redlich-Peterson isotherm models.

The Langmuir isotherm [75] is reliable for monolayer adsorption; it is in accordance with the monolayer envelopment and homogeneous adsorbent surface assumption, represented by Eq. (7):

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e},
\]

where

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e},
\]
where $q_m$ (mg/g) is the monolayer adsorption capacity, and $K_L$ (L/mg) is an isotherm constant related to the free energy of adsorption.

The Langmuir isotherm can be defined using a dimensionless constant separation factor $R_L$ [76] that is given by Eq. (8):

$$R_L = \frac{1}{1 + \frac{bC_0}{K_L}}.$$  

(8)

where $C_0$ (mg/L) is the highest initial concentration of adsorbate, and $b$ (L/mg) is Langmuir constant.

The value of $R_L$ shows the adsorption process which may be undesirable ($R_L > 1$), linear ($R_L = 1$), desirable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm [77] is an experimental model. It is in accordance with the hypothesis of multi-layer adsorbate structure formation onto an adsorbent’s heterogeneous surface. In addition, it is considered that the binding strength reduces through the enhancement of the site occupation and is expressed by Eq. (9):

$$q_e = K_F (C_e)^n.$$  

(9)

where $K_F$ (mg/g(mg/L)$^n$) and $n$ are Freundlich isotherms related to the adsorption capacity and adsorption intensity, respectively.

The Templkin isotherm [78] is in accordance with the supposition that the adsorption heat declines linearly with surface envelopment, because there is an interaction between adsorbate and adsorbate. It is explained by Eq. (10):

$$q_e = Bln(K_TC_e).$$  

(10)

where $B = RT/b$, $b$ (J/mol) is the isotherm constant and related to the heat of adsorption; $R$ (8.314 J/mol.k) is the universal gas constant; $T$ (K) is the absolute temperature; $K_T$ (L/g) is the Templkin isotherm constant which is related to the most binding energy.

The numerator and denominator of Redlich-Peterson isotherm equation have a linear and an exponential relationship with the adsorbate concentration, respectively. It is given by Eq. (11):

$$q_e = \frac{K_{RP}C_e}{1 + a_{RP}C_e^\beta}.$$  

(11)

where $K_{RP}$ (L/g), $a_{RP}$ (L/mg)$\beta$, and $\beta$ are the isotherm parameters. $K_{RP}$ is related to the adsorption capacity, and $\beta$ is related to the adsorption nature. For $\beta = 1$, Eq. (11) converts to the Langmuir equation [79].

The 2,4-D adsorption equilibrium data fit the isotherm models by nonlinear regression over the experimental data, and the main results are presented in Figure 9 and Table 4.

The comparison of $R^2$ and RMSE values among the four models indicates that the Redlich-Peterson is an appropriate isotherm to fit the 2,4-D experimental adsorption data onto the AC, Fe$^0$/AC, TiO$_2$/AC and Fe$^0$/TiO$_2$/AC adsorbents. The amount of $\beta$ that is close to 1 represents the Langmuir isotherm which is also suitable; moreover, $R^2$ and RMSE values of the Langmuir and Redlich-Peterson isotherms are close together according to the data in Table 4. Therefore, the Langmuir isotherm fits the experimental data, showing a homogeneous distribution of active sites on the surface of adsorbents and the monolayer adsorption mechanism. In addition, $R_L$ value is determined to be within 0 and 1 for all the adsorbents and at all pHs, illustrating a desirable adsorption. The monolayer adsorption capacities for AC, Fe$^0$/AC, TiO$_2$/AC, and Fe$^0$/TiO$_2$/AC are 86.5, 87.5, 86.57, and 88.76 mg of adsorbate/g of adsorbent, respectively, at pH = 4.

Table 5 illustrates an evaluation of the monolayer adsorption capacity of 2,4-D with different types of activated carbon adsorbents [180], and the results of this study are compared with the previous studies. According to the obtained monolayer adsorption capacity, it can be concluded that the adsorbents’ capacity of this study can be comparable to the adsorbents’ capacity of the previous studies.

4. Conclusion

Fe$^0$/AC, TiO$_2$/AC, and Fe$^0$/TiO$_2$/AC adsorbents adsorbed 2,4-D without any adsorption capacity reduction as compared to AC. The adsorption equilibrium data better fitted the Langmuir isotherm. The kinetic results indicated that the pseudo-first-order kinetic model managed to describe the adsorption process perfectly. By an increase in the solution pH from
Table 4. Isotherm parameters for the adsorption of 2,4-D at 25°C and pH = 4, 7, 10.

<table>
<thead>
<tr>
<th>pH value</th>
<th>Isotherm model</th>
<th>Parameter</th>
<th>AC</th>
<th>Fe⁰/AC</th>
<th>TiO₂/AC</th>
<th>Fe⁰/TiO₂/AC</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>$K_L$ (L/mg)</td>
<td>0.2178</td>
<td>0.2738</td>
<td>0.263</td>
<td>0.3188</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_m$ (mg/g)</td>
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<td>88.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_L$</td>
<td>0.0490-0.23</td>
<td>0.039-0.196</td>
<td>0.04-0.202</td>
<td>0.034-0.173</td>
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<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.955</td>
<td>0.9942</td>
<td>0.9907</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>RMSE</td>
<td>1.6076</td>
<td>1.8986</td>
<td>2.3829</td>
<td>3.3203</td>
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<tr>
<td></td>
<td></td>
<td>$K_F$ (mg/g)(mg/L)$^n$</td>
<td>21.04</td>
<td>23.37</td>
<td>22.42</td>
<td>25.2</td>
</tr>
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<td></td>
<td>Freundlich</td>
<td>$n$</td>
<td>2.356</td>
<td>2.377</td>
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<td>2.379</td>
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<td>RMSE</td>
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<td>Tempkin</td>
<td>$K_T$ (L/g)</td>
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<td>3.205</td>
<td>2.909</td>
<td>3.903</td>
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<td></td>
<td></td>
<td>$B$</td>
<td>17.55</td>
<td>18.08</td>
<td>18.25</td>
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<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9871</td>
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<td>RMSE</td>
<td>2.7182</td>
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<td>2.1741</td>
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<td></td>
<td>Redlich-Peterson</td>
<td>$K_{RP}$ (L/g)</td>
<td>25.16</td>
<td>32.43</td>
<td>32.25</td>
<td>44.85</td>
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<td></td>
<td></td>
<td>$a_{RP}$ (L/mg)$^β$</td>
<td>0.4662</td>
<td>0.5877</td>
<td>0.6333</td>
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<td>$β$</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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<td>0.2281</td>
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<td>0.2738</td>
</tr>
<tr>
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<td>$q_m$ (mg/g)</td>
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<td>86.78</td>
<td>86.47</td>
<td>88.15</td>
</tr>
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<td></td>
<td></td>
<td>$R_L$</td>
<td>0.055-0.259</td>
<td>0.038-0.196</td>
<td>0.045-0.222</td>
<td>0.029-0.153</td>
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<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9981</td>
<td>0.9953</td>
<td>0.9966</td>
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</tr>
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<td></td>
<td>RMSE</td>
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<td>2.5186</td>
</tr>
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<td></td>
<td></td>
<td>$K_F$ (mg/g)(mg/L)$^n$</td>
<td>19.54</td>
<td>21.35</td>
<td>20.54</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$n$</td>
<td>2.311</td>
<td>2.341</td>
<td>2.322</td>
<td>2.352</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.9727</td>
<td>0.9814</td>
<td>0.9796</td>
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</tr>
<tr>
<td></td>
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<td>RMSE</td>
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<td>3.2948</td>
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<td></td>
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<td>$K_T$ (L/g)</td>
<td>2.158</td>
<td>2.752</td>
<td>2.483</td>
<td>3.35</td>
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<td>Templkin</td>
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<td>17.92</td>
<td>17.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
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<td>0.9800</td>
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</tr>
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<td></td>
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<td></td>
<td>Redlich-Peterson</td>
<td>$K_{RP}$ (L/g)</td>
<td>18.1</td>
<td>27.02</td>
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<td>36.59</td>
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<tr>
<td></td>
<td></td>
<td>$a_{RP}$ (L/mg)$^β$</td>
<td>0.268</td>
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<tr>
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<td>$β$</td>
<td>0.9306</td>
<td>0.842</td>
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<td>0.9987</td>
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</tr>
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</table>
Table 4. Isotherm parameters for the adsorption of 2,4-D at 25°C and pH = 4, 7, 10 (continued).

<table>
<thead>
<tr>
<th>pH value</th>
<th>Isotherm model</th>
<th>Parameter</th>
<th>Adsorbent</th>
<th>AC</th>
<th>Fe(^0)/AC</th>
<th>TiO(_2)/AC</th>
<th>Fe(^0)/TiO(_2)/AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Langmuir</td>
<td>(K_L) (L/mg)</td>
<td>0.1614</td>
<td>0.186</td>
<td>0.1692</td>
<td>0.2205</td>
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<tr>
<td></td>
<td></td>
<td>(q_m) (mg/g)</td>
<td>85.71</td>
<td>86.27</td>
<td>86.19</td>
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<td></td>
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<td>(R_L)</td>
<td>0.064-0.29</td>
<td>0.056-0.264</td>
<td>0.062-0.283</td>
<td>0.018-0.23</td>
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<td>(R^2)</td>
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<td>0.9921</td>
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<td></td>
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<tr>
<td>7</td>
<td>Freundlich</td>
<td>(K_F) (mg/g)(mg/L)(^n)</td>
<td>17.49</td>
<td>19.18</td>
<td>18.13</td>
<td>21.24</td>
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<tr>
<td></td>
<td></td>
<td>(n)</td>
<td>2.224</td>
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<td>Tempkin</td>
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<td>1.721</td>
<td>2.237</td>
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<tr>
<td></td>
<td></td>
<td>(B)</td>
<td>18.35</td>
<td>17.7</td>
<td>18.15</td>
<td>17.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(R^2)</td>
<td>0.9909</td>
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<td>0.9866</td>
<td>0.9810</td>
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</tr>
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<td></td>
<td>RMSE</td>
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<td>3.1784</td>
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<td>3.3295</td>
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<td></td>
<td>Redlich-Peterson</td>
<td>(K_R P) (L/g)</td>
<td>14.93</td>
<td>20.16</td>
<td>16.16</td>
<td>25.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(a_{RP}) (L/mg)(^{\beta})</td>
<td>0.2085</td>
<td>0.3584</td>
<td>0.2359</td>
<td>0.4561</td>
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<td></td>
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<td>(\beta)</td>
<td>0.9462</td>
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<td></td>
<td></td>
<td>(R^2)</td>
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<td>0.9938</td>
<td>0.9954</td>
<td>0.9943</td>
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<td>1.4627</td>
<td>2.1236</td>
<td>1.7979</td>
<td>2.1104</td>
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</table>

Figure 9. Plots of isotherm models for the adsorption of 2,4-D onto: (a) AC, (b) Fe\(^0\)/AC, (c) TiO\(_2\)/AC, and (d) Fe\(^0\)/TiO\(_2\)/AC (pH = 4, adsorbent = 1 g/L, T = 25°C and agitation speed = 130 rpm).
Table 5. Comparison of monolayer adsorption capacity of 2,4-D onto various activated carbon.

<table>
<thead>
<tr>
<th>AC type</th>
<th>Condition</th>
<th>BET Surface area (m²/g)</th>
<th>qₘ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP21</td>
<td>50-100 mg/L, 25°C</td>
<td>427.8</td>
<td>51.02</td>
<td>[1]</td>
</tr>
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<td>AZ21</td>
<td>50-100 mg/L, 25°C</td>
<td>453.8</td>
<td>59.77</td>
<td>[1]</td>
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<td>AN13</td>
<td>50-100 mg/L, 25°C</td>
<td>498.9</td>
<td>80</td>
<td>[1]</td>
</tr>
<tr>
<td>Sesame Stalk (SSAC)</td>
<td>100-500 mg/L, 20°C</td>
<td>490</td>
<td>49.02</td>
<td>[80]</td>
</tr>
<tr>
<td>Powder (PAC)</td>
<td>15-90 mg/L, 25°C</td>
<td>447.7</td>
<td>86.5</td>
<td>This study</td>
</tr>
<tr>
<td>Fe⁰/AC</td>
<td>15-90 mg/L, 25°C</td>
<td>364.6</td>
<td>87.7</td>
<td>This study</td>
</tr>
<tr>
<td>TiO₂/AC</td>
<td>15-90 mg/L, 25°C</td>
<td>447.2</td>
<td>86.57</td>
<td>This study</td>
</tr>
<tr>
<td>Fe⁰/TiO₂/AC</td>
<td>15-90 mg/L, 25°C</td>
<td>402.1</td>
<td>88.76</td>
<td>This study</td>
</tr>
</tbody>
</table>

Cᵢ Thickness of boundary layer  
qₘ Maximum adsorption capacity (mg/g)  
Kₗ Langmuir isotherm constant (L/mg)  
Rₛ Separation factor  
Cₒ Highest initial concentration of adsorbate (mg/L)  
n Freundlich isotherm constant  
Kₚ Freundlich isotherm constant (mg/g(µg/L)ⁿ)  
B Temkin isotherm constant  
b Isotherm constant (J/mol)  
R Universal gas constant (J/mol.K)  
T Absolute temperature (K)  
Kₘ Temkin isotherm constant (L/g)  
Kₚ Temkin isotherm constant (L/g)  
αₚ Redlich-Peterson isotherm constant (L/mg)  
β Redlich-Peterson isotherm constant  
E Efficiency (%)  

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Nomenclature

2,4-D 2,4-dichlorophenoxyacetic acid  
t Contact time (min)  
qₜ Adsorption capacity at time t (mg/g)  
Cₒ Initial concentration of pollutant (mg/L)  
Cₜ Concentration at t (mg/L)  
V Volume of the pollutant solution (L)  
m Mass of the adsorbent (g)  
Cₑ Equilibrium concentration of pollutant (mg/L)  
k₁ Pseudo-first-order kinetic rate constant (1/min)  
qₑ Equilibrium adsorbed 2,4-D on the adsorbent (mg/g)  
k₂ Pseudo-first-order kinetic rate constant (g/mg min)  
R² Correlation coefficient  
RMSE Root-Mean Square Error  
kₐ Intraparticle diffusion rate constant (mg/g min⁰.⁵)  

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