Diclofenac removal from wastewater by activated carbon

Ghayda Y. AL-Kindi\textsuperscript{1}, Faris H. AL Ani\textsuperscript{1}, Noor Kh Al-Bidri\textsuperscript{2} and Husam A. Alhaidri\textsuperscript{1}

\textsuperscript{1}University of Technology, Civil Engineering, Baghdad, Iraq.
\textsuperscript{2}Al Rafidain University College, Civil Engineering, Baghdad, Iraq.
Corresponding author: 40126@uotechnology.edu.iq

Abstract. Pharmaceuticals have been widely found in wastewater. Among them, diclofenac was detected at the highest frequency; in this study, the commercial activated carbon was used to remove diclofenac from synthetic wastewater. Various testing methods were applied to evaluate the efficiency of the activated carbon for removing diclofenac from residues wastewater such as scanning electron microscopy (SEM), Brunauer, Emmett and Teller (BET), and Energy Dispersive Spectroscopy (EDS). The operating conditions were determined by using a batch reactor with various parameters such as different pH, diclofenac concentration, and different mass of activated carbon. The result of operations conditions was: pH 5, diclofenac concentration is 1000 mg/l mass of activated carbon is 500gm/L. While, the difference of initial Ibuprofen concentration, flow rate, and bed depth was determined by packed bed reactor, it was found 2cm for bed height, and flow rate 25 l/hr. Diclofenac concentration, 625mg/l. from adsorption equilibrium and with Langmuir and Freundlich models, the kinetic constants were determined, also shown the pseudo-first-order gave the best result, and more suitable for the removal of Diclofenac by adsorbed activation carbon.

Keyword: Batch reactor, Diclofenac, Frundlish, and Langmuir, Kinetic parameter, packed bed reactor.

1. Introduction

As possible bioactive chemicals in the world, pharmaceuticals have been gaining growing attention over the last two decades. Among these drugs, three of the most commonly found in the aquatic setting are diclofenac (DCF), carbamazepine (CBZ) and amoxicillin (AMX) [Teijon, 2008: Ortiz, 2013]. The structure of Diclofenac was seen most commonly and at the highest concentration levels (Fig. 1). This drug is a nonsteroidal anti-inflammatory drug (NSAID) widely used as a potent painkiller that exhibits cyclo-oxygenase (COX) inhibitory action. Although the large margin of safety of Dic. Possible adverse effects of this drug on gastrointestinal, hepatic, renal, and cardiovascular organs have been documented [Bort et al. 1999; Hickey et al. 2001; McGettigan and Henry 2006].

![Figure 1. The structural formula of diclofenac sodium (a) and diclofenac (b).](image-url)
Via distinct paths, pharmaceutical residues are transferred to water circles. Wastewater treatment plants (WWTPs) serve as a pathway to water sources for human pharmaceuticals, while most residues of veterinary pharmaceuticals are directly released into the environment [Ternes, 1998]. Such as rivers, lakes, reservoirs, and aquifers with groundwater for drinking water supply [Ternes and Joss, 2006; Xu et al., 2007]. Several technologies for treating these pharmaceutical compounds from wastewater have been developed over the past decades [Secondes, 2014; Rizzo, 2009]. Biological treatment has been commonly used in activated sludge, but uncompleted diclofenac removal by these methods [Vieno, 2014]. Therefore, several distinct water treatment systems have been used to remove pharmaceuticals, especially technologies using adsorption, advanced oxidation processes (AOPs) using ozone, ultraviolet radiation, gamma radiation, electro-oxidation [Ikehata et al., 2006]. Also, membrane filtration is used, such as nanofiltration and reverse osmosis [Radjenovic et al., 2008; Boleda et al., 2011]. During the analysis of DCF detection in finished water, Eline concluded in 2013 that traditional drinking water treatment followed by GAC filtration was successful in removing DCF (P99.7 percent). Although Al Ani 2019 demonstrates the removal of diclofenac by Al-Fe pillared clay as adsorption, this method successfully removes 99%. In 2019, Gledson recommended the use of polyethylene terephthalate composite (PTC) content, iron oxide (Fe3) functionalised sugarcane bagasse ash (SBA) (PTCSBA/Fe3) in the adsorption of diclofenac sodium (DIC) 1000 μg L-1 in synthetic solution, due to the low cost of the composite. The various removal methods include membrane filtration, ozonation, advanced oxidation, Fenton oxidation, electrochemical oxidation, photocatalysis, soil aquifer treatment, ion exchange, and adsorption. remove of diclofenac from wastewater are studied in Fatemeh, 2020. It concluded that in the case of wastewater treatment, adsorption is considered more efficient and cost-effective than other approaches. Nguyen, 2020 Porous graphitic biochar has been synthesised with potassium ferrate (K2FeO4) as an activator for both carbonisation and graphitisation processes to remove diclofenac from drinking water by one-step biomass treatment. And Fe@BC was found to be a promising absorber for DCF removal from water and water purification applications by chemical adsorption. The purpose of this study is to test the properties of commercial activated carbon as an adsorbent to remove diclofenac drug residues from manciple wastewater.

2. Experimental work
2.1 Materials and methods
1- The Diclofenac tablet drug from the pharmacy was used in the preparation of syntheses wastewater. Still, the blank Diclofenac was brought from the Samarra pharmaceutical factory, used preparation the calibration curve in the High-Performance Liquid Chromatography (HPLC) instrument, Germany, YL 9100 HPLC System, Detector with C18 column. The mobile phase was programmed at a 1.2 ml/min flow rate
2- The Diclofenac solution was prepared in four concentrations using 100- 250-500-1000 (gm.) of Diclofenac after cracking with plastic mortar in 1 L of distilled water.
Activated Carbone was a commercial type obtained from the local market; his characteristic show in Table (1). The surface area and pore size were examined for activated Carbone by BET Instrument.

| Table 1. Characteristic of activated carbon |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| SI No | Parameters | units | Report Value | Specification | Testing code |
|-------|------------|-------|---------------|---------------|-------------|
| 1 | Iodine number | Mg/gm | 1027 | 1000 min | ASTM D 4607 |
| 2 | Moisture | % | 4.86 | 5.0 max | ASTM D 2867 |
| 3 | Ash | % | 4.83 | 5.0 max | ASTM D2666 |
| 4 | Apparent Density | Gm/ml | 0.52 | 0.40-0.55 | ASTM D2854 |
| 5 | pH | 9.2 | 7-10 | ASTM D3838 |
| 6 | Oversize | % | 4.12 | 5.0 max | ASTM D2862 |
| 7 | Undersize | % | 2.69 | 5.0 max | ASTM D3802 |
| 8 | Ball-Pan hardness | % | 99.38 | 96 min | ASTM D3802 |
2.2 Experimental procedure
In this analysis, the batch reactor and packed bed reactor were used to define the operating state, also from the results of the batch reactor, the kinetic parameter was calculated. In contrast, the isotherm model with different parameters was studied in the packed bed reactor to calculate the kinetic isotherm model.

2.2.1 Batch Experiments. Deferent parameter (pH, the mass of adsorption (activated Carbone), diclofenac concentration) were studied in the Batch reactor. The 100mg/l of Diclofenac solution placed in 4 beakers, as shown in Figure 2. The operation conditions were kept constant at pH 7 and temperature at 22 oC. The activated carbon was applied with different mass (100, 250, 500, and1000 mg). The jar test instrument was used with rotation (200 rpm) for 3 hr. the samples were takin each 30min, then filtered and analysed.

In the second part, the same procedure was used except the variable is Different masses of Diclofenac (100, 250, 500, and1000 mg) and constant activated Carbone (100mg/l)

In the third part, using constant Diclofenac concentration 100mg/l and activated Carbone 100mg. While the experiment was done in the same manner. All samples were examined about diclofenac by the HPLC instrument.

2.2.2 Packed Bed Reactor Experimental.

1. Reactor description
The Packed bed reactor has a glass tube length of (60) cm and an inner diameter of (2.1) cm. The glass beat's different size was also used to provide the inert zone to avoid any lost adsorbent from the bed. Some of the devices used, such as valves, flow meters, pumps, are also used, and the packed bed reactor used in this work is shown in Figure 3.

![Figure 3: Schematic diagram of the packed bed system](image-url)
2. Experimental procedure
From the result which obtained from batch reactor pH 7, temperature 22°C, the experiments were done in different bed height (1, 1.5, and 2 cm), different initial Diclofenac concentration (100, 400, and 625 mg/l), and different flow rate (25, 30, and 35) l/hr.

The adsorbent was packed in the adsorption column for certain bed height. The Diclofenac solution was put in a feed tank and pumped from top to bottom packed bed through the flow meter to controlled flow to the collection tank. The samples were withdrawn from effluent every 30 minutes, and then filtered analysed by HPLC instrument.

3. Result and discussion
3.1 BET Instrument Results
The commercial activated Carbone was measured by BET Instrument, and the results show in Table 2 show the activated carbon has a high surface area. For pore size according to the International Union of Pure and Applied Chemistry (IUPAC) classification of pore size (Å) as macropore (≥ 500), mesopore (20 to 500) supermicropore (7-20) and ultramicropore (≤ 7) [NICOLETA, et al., 2013]. From the results, show activated carbon have macropore. The results show the Pore volume of activated Carbone before and after use in a packed bed reactor.

| adsorbent          | Surface area (m²/gm) | Pore volume cm³/gm | Pore size (Å) |
|--------------------|----------------------|--------------------|---------------|
|                    | before               | after              | before        | after          | after          |
| activated carbon   | 890                  | 0.7935             | 0.9788        | 2.17 nm        |

The results of Energy Dispersive Spectroscopy (EDS) for activated carbon before used in the processes of packed bed reactor, (b) after the Diclofenac treatment in the packed bed reactor, were shown in Figure 4 a-b, the amount of carbon reduces after adsorption in packed bed reactor, also found a quantity of potassium and sodium adsorb on activated carbon after Diclofenac treatment in the same reactor.

Figure 4: EDS results for (a) activated carbon before and (b) after the process of packed bed reactor

the images of the activated carbon before and after the Diclofenac treatment in packed bed reactor by the scanning electron microscopy (SEM) test are shown in Figure 5 a-b (a) for commercial activated carbon, (b) after treatment in packed bed reactor, the large gaps in the activated carbon became small gaps, also the emergence of clear layers during different magnification.
Many factors were studied (pH, Diclofenac concentration, the mass of activated Carbone). In the first parameter (different Diclofenac concentration), the temperature was kept constant 22°C, pH 7, and 100g of activated Carbone. Only the concentration of Diclofenac was a change (100, 250, 500, 1000mg/l). The results showed the relation between time in min. And the concentration (mg/l) in Figures (5), and the Diclofenac removal efficiency in Figure (6), the concentration of diclofenac decrease with time, The reaction in figure 6 show the efficiency removal increase during 75min then reach to study state, due to the reaction between drug and adsorption. The efficiency removal calculate from ((initial concentration – final concentration)/ initial concentration)*100.

The temperature and pH kept constant only used differently in activated carbon. The temperature (22°C) and pH (7) were still unchanged, with the concentration of diclofenac (100) mg / l and the concentration of adsorbents altered. Figure 7 indicate that the concentration of Diclofenac decreases with time. Figure 8 indicate an improvement in the removal of Diclofenac with an increase in the adsorbent mass at less time. Also, to increase removal efficiency with a decrease in adsorbent masses, activated carbon reaction is very rapid at first, then continues slowly until it reaches a steady-state. This process may be due to an increase in surface area; the removal of Diclofenac increases further.
Figure 7: The relation between time and Diclofenac concentration using activated carbon, with constant temperature 22°C, pH7, and Diclofenac concentration (100mg/l).

Figure 8: The removal efficiency of Diclofenac using activated carbon, with constant temperature 22°C, pH7, and Diclofenac concentration (100mg/l).

Experiments were carried out to research the influence of pH on the removal of diclofenac and the maintenance of other parameters, such as temperature (22)°C, mass concentration of adsorbents (100 mg/l), and concentration of diclofenac (100 mg/l). Figure 9 displays the results for activated carbon; the concentration of diclofenac decreased over time, suggesting the continuous removal phase over experimental time. Diclofenac Figure 10’s removal efficiency indicates that pH changes at close levels impair the efficiency of removing Diclofenac from activated carbon. With increasing pH, these removals decreased. It was found that the adsorption was highly dependent on the pH solution, which affects the adsorbent’s surface charge and the adsorbate’s degree of ionisation and speciation. More protons would be accessible at lower pH; the increasing electrostatic attraction between negatively charged Diclofenac and positively charged adsorption sites and triggering an increase in adsorption of Diclofenac potassium; these results are consistent with Lombardi (2003) findings. The activated carbon steady state (150) min.

Figure 9. The relation between time and Diclofenac concentration using different pH, with constant temperature 22°C, pH7, activated carbon adsorbent (100 mg/l) and Diclofenac concentration (100mg/l).

Figure 10. The removal efficiency of Diclofenac using different pH, with constant temperature 22°C, pH7, activated carbon adsorbent (100 mg/l) and Diclofenac concentration (100mg/l).

d- The kinetic constants
the kinetic constants were determined by the kinetic equation as in equation 1 (Wang, 2008).

\[
\frac{dc}{dt} = - k C^n
\]  

(1)
Where,
\( k \) = adsorption coefficient,
\( C \) = diclofenac concentration,
\( t \) = time, and
\( n \) = reaction order.

The pseudo-first and pseudo-second-order kinetic equations were used to determine the kinetic constant, as in Equations (2) (3), respectively (Emami et al., 2010):

\[
(\text{First – order}) \quad \log (q_t - q_e) = \log q_e - K_1 t
\]

(2)

\[
(\text{Second-order}) \quad \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

(3)

Where:

- \( q_t \) = adsorption at time \( t \).
- \( q_e \) = adsorption at equilibrium (mg / g).
- \( T \) = time of adsorption phase (min),
- \( k_1 \) and \( k_2 \) are the rate constant of pseudo-first and pseudo-second-order reaction respectively.

To determine \( K_1 \) in \( \text{min}^{-1} \) plotted \( \ln (q_e/q_t) \) as opposed to \( t \).

\[
\text{(Second-order)} \quad \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

(3)

The initial sorption rate determined by the following equation to:

\[
h = k_2 q^2
\]

(4)

The kinetic analysis of diclofenac removal in a batch reactor was dependent on various concentrations of diclofenac because of the high R2. which used in the first and second-order, the Figures (11), (12) were shown the kinetic results, also in Table (3).

**Figure 11:** The pseudo-first-order kinetic plots for the adsorption of Ibuprofen concentration on activated carbon.

**Figure 12:** The pseudo-second-order kinetic plots for the adsorption of Ibuprofen concentration on activated carbon.
Table (3) Results of Kinetic data

| Kinetic (Pseudo-first-order) | Kinetic (Pseudo Second-order) |
|-----------------------------|-------------------------------|
| R2  | k1 (min⁻¹) | Calculated eqilb. qe (mg/g) | k2 (g/mg.min⁻¹) | h (mg g⁻¹ min⁻¹) | R2  | Calculated eqilb. qe (mg/g) |
|-----|-------------|-------------------------------|-----------------|------------------|-----|-------------------------------|
| 100 | 0.934       | 0.0026                        | 691.3           | 0.0005           | 31.25 | 0.153                        | 250 |
| 250 | 0.8286      | 0.0014                        | 794.3           | 0.3757           | 146.75 | 0.8024                       | 625 |
| 500 | 0.7153      | 0.0025                        | 410.2           | 0.1032           | 161.25 | 0.6779                       | 1250|
| 1000| 0.7643      | 0.0027                        | 289.1           | 0.2011           | 1256  | 0.6577                       | 2500|

Different bed heights of adsorbent (1, 1.5, and 2 cm) with constant concentrations of diclofenac (625) mg/l were used in the packed bed reactor during the experiment phase. The flow rate remained constant (25 l/hr.), pH (7) because of the effects of pH and temperature (22°C) differed slightly. The breakthrough curves are seen in Figures 13, while the concentration of Diclofenac differs with time in Figures 14.

The results show that breakthrough increased with increasing bed height, it also shows that the breakthrough observes clearly and easily in bed height (1) cm, which means that the bed saturated very quickly. Still, the breakthrough requires more time in (1.5) and (2) cm bed height because smaller height has a smaller capacity to adsorb the Diclofenac solution. These findings comply with What [Al Ani, 2019] inferred.

For all bed heights, the breakthrough starts at about the same time but finishes at a different time. The contact time between adsorbate and bed increases with increasing bed height so that the removal effectiveness also increases because there is enough space and pores. Compared with other bed heights, the best height shown in the figures is (2) cm. Additionally, It is evident from the figures that during the experimental period, the removal efficiency of bed (2) cm is not completed and can extract additional higher concentrations and concentration of Diclofenac.

**Figure 13:** Breakthrough curve of Diclofenac adsorption on activated carbon column with different depth at a flow rate of 25 l/hr., pH 7, and temperature 22°C.

**Figure 14:** Adsorption of Diclofenac on activated carbon column with different depth at a flow rate of 25 l/hr., pH 7, and temperature 22°C.
bed, so that resident time decreases with an increase in flow rate. Figures (16) also show that the concentration of Diclofenac decreases with time and the operating time of the bed for removal increases with a decreasing flow rate.

The effect of using variable initial Diclofenac concentration (250, 500, and 625) mg/l on the breakthrough with other parameters kept constant were also studied, and the results show in Figure (17). The bed height was (2) cm, flow rate (25) l/hr, pH 7, and temperature 22°C. Results indicate that the breakthrough increased as concentration-increased shown in Figure (18).

**Figure 15.** Breakthrough curve of Diclofenac adsorption onto activated carbon at different flow rates with depth 2cm, pH 7, temperature 22°C, and Diclofenac concentration 625mg/l.

**Figure 16.** Diclofenac adsorption on activated carbon at different flow rates with depth 2cm, pH 7, temperature 22°C, and Diclofenac concentration 625mg.

**Figure 17.** Breakthrough curve of Diclofenac adsorption onto activated carbon with different concentrations at depth 2cm, pH 7, and temperature 22°C.

**Figure 18.** Diclofenac adsorption on activated carbon for different concentrations at depth 2cm, pH 7, and temperature 22°C.

**Kinetic isotherm model**

The isotherm analysis was studied during a fitting technology, for many isotherms models to choose the suitable model to apply for design objectives, so that the equation 5 were used to determine the constant of Freundlich adsorption models.

\[ \ln q_e = \ln K + \frac{1}{n} \ln C_e \]  

Where k, n constant, \( \frac{1}{n} \) the range between (0-1)
The equation (6) used to determine the Langmuir constant, by slope and interest linearised
\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} \cdot b} \cdot \frac{1}{C_e}
\]  

(6)

the value of qmax (mg/g) and b (l/mg) which determine by using this equation through plot 1/qe versus 1/Ce. For Frundlish adsorbent adsorption model, pH was fixed at (5), which giving higher removal efficiency and the other parameters remained constant, only the Diclofenac concentration was changed. The Results indicated that change in Diclofenac concentration has more effect on Diclofenac removal and the concentration of (1000) mg/l gives higher R2 of (0.979) as shown in Figures (19), so that, the kinetic adapted on change in Diclofenac concentration.

Applying the Langmuir adsorption model with the same above parameters gives the best removal at (1000) mg/l with R2 (0.991). The kinetic is shown in Figure (20). The values of the Frundlich and Langmuir models constants are shown in Table 4.

![Figure 19: Frundlich mode for activated carbon adsorbent.](image1)

![Figure 20: Langmuir mode for activated carbon adsorbent.](image2)

Table 4. constants of the Frundlich and Langmuir models

| Adsorbion material | models         | constant Model | R² | K    | n  |
|-------------------|----------------|----------------|----|------|----|
| Activated Carbon | Frundlish model| 0.979          | 0.66 | 6    |
|                   | Langmuir model | to 0.991       | Q=41 | B=0.12 |

4. Conclusion
The conclusions taken from this review are: Activated carbon enhances the clearance of diclofenac and enters the steady-state in 75 minutes. And its efficiency in removing high concentrations has been proved because adsorbents are highly efficient, and removal efficiency increase with the increase in adsorbent mass. The optimum operating conditions for removing diclofenac were found to be pH = 5, activated carbon concentrations were 100 mg / l, and diclofenac concentrations were 100 mg / l. The first and second pseudo order were used to determine the kinetic parameter according to the strong R2. The contact time between the adsorbent and the bed increases with the increase in bed height. The removal efficiency increases due to the existence of sufficient room and sufficient space. Compared to other bed heights, the best height was (2) cm, the Langmuir adsorption model gives the best removal at (1000) mg/l with R2 (0.991).
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