Removal of Therapeutic Drug *Diclofenac* Pollution by the Acid Digested Carbon of Waste Leathers

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ABSTRACT

By manipulating the physico-chemical conditions, the adsorption characteristics study on the removal of the therapeutic drug *Diclofenac* on the Acid Digested Carbon of waste Leather (ADCL) were analysed. The smallest particle size affords the most surface area and more adsorbed material (92.43% for 0-63 micron). The adsorption of *Diclofenac* on this acid-digested carbon of waste leather required acidic pH ranges. Nevertheless, different adsorbates preferred various acidic pH ranges between 1 and 6. In this instance, 92.15% of adsorption occurs at pH 5. The results of this study revealed that the percentage of diclofenac adsorption is directly proportional to the dosage and contact time of the adsorbent and inversely proportional to the initial concentration of the adsorbate. Due to the absence of a chemical bond forming between the adsorbent and adsorbate, the order of this adsorption is pseudo-second order kinetics, and therefore falls under the category of physisorption. For these experiments, the freundlich and Langmuir isotherm model is appropriate. The thermodynamic analysis shows negative $\Delta G^\circ$ and positive $\Delta H^\circ$ and $\Delta S^\circ$ values, indicating that this adsorption is, respectively, spontaneous, practicable, and physical in character. The FT-IR, SEM, and XRD spectrum data support the above experimental findings.

Keywords: Therapeutic drugs, Adsorption, Isotherm, Kinetics, Thermodynamics and Spectrum.

INTRODUCTION

One of the industrial sectors that is growing most quickly is the pharmaceutical one. Pharmaceutical and personal care product (PPCP) production and consumption have both been rising steadily. This causes these toxins to pollute the environment. Non-steroidal anti-inflammatory medicines (NSAIDs), antibiotics, estrogens, beta-blockers, lipid metabolism regulators, and antiepileptic pharmaceuticals are the drugs most frequently found as pollutants in aquatic environments¹. These medications are utilised in medicine, veterinary medicine, and animal husbandry and are thereby released into the environment from a variety of sources. They arrive at wastewater treatment facilities along with wastewater from homes, health facilities, hospitals,
and outpatient clinics, and after treatment, they discharge sewage into surface waters. Due to their consumption in the reproduction of cattle, these toxins are dispersed into the ground and areas close to surface or groundwater, for instance. Another source is fish farming, which directly delivers drugs into the water. Diclofenac now present in drinking water as a result of this compound's contamination of surface water and some groundwater. Diclofenac is not completely removed by conventional water treatment facilities. Adsorption, biodegradation, photolysis, membrane processes, ozonation, combination O$_2$/H$_2$O$_2$ approach, and activated sludge adsorption are the techniques used to successfully remove diclofenac from water or sewage. Advanced ozonation techniques can be risky as well as expensive, despite the fact that they are effective. Most of the unidentified intermediate ozonation products, which are frequently more poisonous than the starting chemicals, are formed more quickly with this technique. Adsorption is an extremely efficient and reasonably priced approach that doesn't pollute additional water sources. As a result, adsorption is currently being studied quite a bit in relation to the removal of medicines, including Diclofenac. According to the pH, temperature, and dose of the solution, this study tried to find out how well Diclofenac sodium adsorbed on three distinct kinds of commercial activated carbon used in water treatment facilities. In order to clarify the research's conclusions, various adsorption kinetics and statics models will be used.

MATERIALS AND METHODS

Adsorption experiments

The studies were conducted at 30°C, with 0.1M HCl and 0.1M NaOH used to change the acidic and basic properties of the solution. The adsorbent and adsorbates were allowed to come into contact with each other for a set amount of time to allow for adsorption, and the amounts of adsorbent and adsorbates were recorded. For this experiment, a 100 mL stopper bottle was used, and the mixture was agitated for 180 min with a mechanical shaker set to the right rpm (100-300). It is filtered after the equilibrium with watt man 40 filter paper and filtered. A UV-spectro photometer set to a suitable filter range was used to check the drug adsorbent solution Con. in the filtrate. The experiment was performed with the physical and chemical parameters changed, and the adsorbate volume was 50 mL.

\[
\text{Adsorption(\%) = } \frac{(C_o - C_e) \times 100}{C_o} 
\]

Where $C_o$ is the IC is initial Con. and $C_e$ is the Con. of the drug adsorbate at equilibrium.

Effect of adsorbent dosage

The effect of effect of adsorbent dosage was investigated using adsorbent ranging from 50 to 250 mg in a 50 cm$^3$ drug adsorbate solution (50 mg dm$^{-3}$). The percentage of adsorption in each case was calculated while keeping all other variables constant. The top-quality value for adsorbent dosage was determined as a result of this, and it was used in all batch experiments.

Effect of pH

The effect of pH on drug adsorbate adsorption on the adsorbent was investigated by equilibrating 50 cm$^3$ of drug adsorbate solution (50 mg dm$^{-3}$) at pH values ranging from 1 to 6, while keeping all other variables constant. The ideal pH was then determined and used in all subsequent adsorption trials. Using a digital pH metre, the pH of the samples was determined. 4 and 9.2 buffers were employed to calibrate the pH metre.

Effect of initial concentration

At room temperature (30°C), the adsorption studies were done in a batch approach. A known weight of adsorbent fabric was added to 50 mL of drug adsorbate solution with an IC of 10 mgL$^{-1}$ to 60 mgL$^{-1}$ while all other factors were kept constant. After equilibrium was determined, the percentage of adsorption for each value of preliminary concentration was determined.

Effect of contact time

The effect of contact time between the adsorbent and the adsorbate was determined by conducting the experiment at different contact times ranging from 30 to 180 min, while keeping particle size, preliminary Con., AD, pH, and temperature constant. Each experiment was repeated three times to increase the accuracy of the data, and average results were utilised to generate the graphs.

Effect of temperature

The adsorption studies were carried out in a thermostat shaker (Remi, India) at four distinct temperatures, namely 30, 40, 50, and 60°C, while keeping all other variables constant.
Temperature fidelity was previously maintained with an accuracy of 0.5°C.

Effect of particle size
For checking the most adsorption of drug adsorbate, the impact of adsorbent size of particle measurement was tested in the range of 0-200μ microns particle dimension (0-63μ, 63-125μ, 125-200μ).

RESULT AND DISCUSSION

Adsorption of Diclofenac
Effect of particle size
ADCL from ADCL was used to study how pore size affects adsorption. By putting it through sieves of these specific diameters, this ADCL is divided into three separate sizes. ADCL with three distinct pore sizes (0–63, 63–125, and 125–200 microns, respectively) was used to test the adsorption of Diclofenac.

Effect of pH
The pH of the medium has a significant impact on the rate of Diclofenac removal by adsorption on ADCL generated from ADCL. The pH range of 1-6 was used for the rate measurement. When the pH was raised from 1 to 6, the rate constant fell (Fig. 3.1.2). The ADCL derived ADCL is always present in salt form in strongly acidic media. This form is filled with positively charged sites that interact with the anionic Diclofenac molecule moiety. At increasing pH levels, the salt form changes into the basic form. As the pH rises, the transition intensifies, depleting the ADCL's active sites. When the pH rises from pH:1 to pH:6, the uptake of Diclofenac increased from 41.05% to 92.15%. The capacity for adsorption, which is 92.15% at pH 5, also noticeably increases.

Effect of adsorbent dosage
The removal rate of Diclofenac gradually improved due to the increases in adsorbent pores and adsorption sites, as evidenced by the quantity of Diclofenac absorption increasing from 63.22% with 50 mg adsorbent to 86.11% with 200 mg adsorbent. When the mass of the adsorbent reached a particular level, the adsorption would gravitate toward equilibrium. With an adsorbent mass of 200 mg and an initial Diclofenac concentration of 10 mg L⁻¹, the removal rate of Diclofenac increased to 98.69%. High adsorbent dosages caused a surface equilibrium state and a decrease in the adsorption capacity per unit mass of adsorbent because there weren't enough Diclofenac molecules in solution to fully mix with all of the effective adsorption sites on the adsorbent Figure 3.1.3.

Effect of initial concentration
With a rise in Diclofenac concentration, the rate of adsorption reduces. The surface of the ADCL is loaded with more Diclofenac molecules at higher Diclofenac concentrations. The ongoing blockage of the active sites on the ADCL surface by the Diclofenac molecules that have already been adsorbed would consequently be expected to result in a slower adsorption. As the concentration of Diclofenac increases from 10 to 60 mg L⁻¹, as shown...
in Fig. 3.1.4, the adsorption capacity declines from 91.31% to 77.77%. The tendency is due to a steady decline in the electrostatic interaction between Diclofenac and the active sites of the absorbent.9.

Effect of Contact Time

The amount of Diclofenac adsorbed onto the ADCL and the amount of Diclofenac desorbing from the adsorbent are in a condition of dynamic equilibrium. The amount of Diclofenac adsorbed at the equilibrium time indicates the maximum adsorption capacity of the adsorbent under those operating conditions, and the time necessary to reach this state of equilibrium is referred to as the equilibrium time. Adsorption rises as contact time rises, peaking at 87.23% after 3 hours. Fig. 3.1.5 demonstrates the smooth and continuous Diclofenac coverage on ADCL. Within 30 min of contact time with the adsorbent, about 61.99% adsorption had occurred, demonstrating the effectiveness of ADCL as an adsorbent.10.

Effect of Temperature

Diclofenac was investigated at a concentration of 10 mgL⁻¹ at various temperatures of 30, 40, 50, and 60°C. The results are graphed in the Fig. 3.1.6. The capacity of Diclofenac to adhere to ADCL increases with temperature. At 30°C, the lowest adsorption was 82.55%, while at 60°C, the highest adsorption was 88.32%. This suggested that the adsorption was an endothermic process that occurred spontaneously. As temperature rose, so did the molecules of Diclofenac's thermal motion, solubility, and chemical potential. Additionally, temperature was directly connected to the pore structure of ADCL. Due to thermal expansion, ADCL's pore structure and number of active adsorption sites grew as temperature rose. These causes are depicted as the reason why Diclofenac's adsorption capability increased with temperature.11.

Kinetic study

The effectiveness of adsorption is a property governed by the kinetics of adsorption. Adsorption was monitored at intervals of 10, 20, 30, 40, 50, and 60 min because the initial sorption rate is critical. Four models, including Lagergren's.

pseudo-first order kinetics in equation: log (qₐ–q)= log qₑ–k₁t/2.303
(2)

pseudo-second order kinetics in equation: t/qₐ=1/k₂. qₑ²+qₑ
(3)

Elovich kinetics in equation: qₐ=1/ In αβ + 1/ Int
(4)

The intra-particle diffusion model in equation; qₐ=kₚ.t¹/²
(5)

Were used to analyse the kinetics of Diclofenac's adsorption on ADCL. The Table 3.1.7, Fig. 3.1.7b. below contains the kinetics parameters. The findings demonstrated that the adsorption of Diclofenac on this ADCL can be described by a pseudo-second-order kinetic model and established that physical adsorption predominated the adsorption process. The adsorption process not only involved the internal diffusion of micropores...
and the liquid film diffusion, but also the physical adsorption process without the sharing of electrons and the weak physical forces between the surface of the ADCL and Diclofenac. Second order kinetics is the best fit, according to the great precision of the $R^2$ values for this model.

**Table 3.1.7 & Figure 3.1.7(a,b): Kinetic parameters for the adsorption of Diclofenac**

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>$K_1$</th>
<th>$q_e$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Order</td>
<td>0.004606</td>
<td>1.26112</td>
<td>0.974</td>
</tr>
<tr>
<td>II Order</td>
<td>3.184713</td>
<td>0.01414</td>
<td>0.99</td>
</tr>
<tr>
<td>Int part diff</td>
<td>0.105</td>
<td>1.476</td>
<td>0.98</td>
</tr>
<tr>
<td>Elovich model</td>
<td>0.458</td>
<td>0.452</td>
<td>0.947</td>
</tr>
</tbody>
</table>

**Langmuir isotherm:** $C_e/X = 1/K'K_e + C_e/K$ \( (6) \)

**Freundlich isotherm:** $\log K_f + (1/n) \log q_e = 4.2 \log q_e C$ \( (7) \)

**Redlich Peterson isotherm:** $q_e = K_n C_e/(1+b_R C_e^\beta)$ \( (8) \)

The Dubinin-Kaganer-Radushkevich Isotherm: $\log q_e = \log X_m - 2/\gamma 2.303$ \( (9) \)

**Table 3.1.8 & Figure 3.1.8(a,b): Isothermal parameters for the adsorption of Diclofenac**

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>$K_L$</th>
<th>$q_e$</th>
<th>$b_L$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L Isotherm</td>
<td>2.985075</td>
<td>21.2766</td>
<td>0.140299</td>
<td>0.865</td>
</tr>
<tr>
<td>F Isotherm</td>
<td>3.67282</td>
<td>1.94932</td>
<td>0.985</td>
<td></td>
</tr>
<tr>
<td>DKR</td>
<td>0.96726</td>
<td>0.521</td>
<td>3.31894</td>
<td>0.94</td>
</tr>
<tr>
<td>RP</td>
<td>0.234</td>
<td>4.2735</td>
<td>0.92308</td>
<td>0.824</td>
</tr>
</tbody>
</table>

**Isothermal study**

The Dubinin-Kaganer-Radushkevich (DKR), Temkin, Freundlich, and Langmuir models were all in good agreement with the results of the adsorption isotherm analysis, but the Langmuir model exhibited higher consistency. These findings supported the Langmuir model's assumption that the Diclofenac adsorption sites of the adsorbent were homogeneous. Because Diclofenac molecules uniformly covered the surface of the ADCL, the adsorption sites were homogeneous. Therefore, it may be assumed that the physical monolayer adsorption was the method used to adsorb Diclofenac by this ADCL. Table 3.1.8, Fig.3.1.8 a&b show the isotherm parameters calculated from the linear plots of equations.

The Langmuir isotherm's sorption equilibrium constant $K_L$ value, or 2.9851 mgg$^{-1}$, demonstrated the strong adsorption capacity of the biosorbent toward Diclofenac adsorption. The values of the dimensionless separation factor $(R_L)$, which are less than one, further support this. According to the correlation coefficient $R^2$ value of 0.865, the Langmuir isotherm is a reliable explanation for Diclofenac adsorption.
The experimental results can be explained by the Freundlich isotherm, according to the computed $R^2$ value for the isotherm, which was determined to be 0.985. The Freundlich isotherm was used to get the ultimate adsorption capacity $K_F$ value, which were 3.67282. The values of the Freundlich constant, $n$, are significantly higher than one, suggesting that physisorption controls the adsorption process. The experimental results may be explained by the Redlich-peterson isotherm, according to the $R^2$ value that was determined for the isotherm, which was found to be 0.824. According to this isotherm’s calculations, the value was 0.234. It was decided to use the Dubinin-Kaganer-Radushkevich (DKR) model to explain the single-solute adsorption isotherms. The experimental results cannot be satisfactorily explained by the DKR isotherm, as shown by the $R^2$ value determined for the DKR isotherm, which was found to be 0.94. According to this isotherm’s calculations, the value was 0.9673. The values of the desorption constant, $\beta$, in the Dubinin-Kaganer-Radushkevich and the Redlich-Peterson isotherms serve as a gauge for the desorption constant. If the values are smaller than one, then the adsorption is likely to be favourable. The sorption energy in the DKR isotherm can be used to distinguish between physisorption and chemisorption. Lower values suggest that physisorption is more common, hence it is generally thought to indicate a satisfactory adsorption process when the value of $1/n$ is in the range of 0.1 to 1.0. Since the experiment's index value was within the allowed range, the adsorption process seemed to be functioning well.

**Thermodynamic study**

Analysis of the thermodynamics of ADCL adsorption was done from an energy standpoint. Adsorption thermodynamics analysis of the driving force of adsorption revealed whether the process was spontaneous or not. The negative $\Delta G^\circ$ values, which are visible in Table 3.1.9 in terms of feasibility and spontaneity, were used to illustrate the discolored process of diclofenac on ADCL. The positive $\Delta H^\circ$ values at various temperatures show that the adsorption was an endothermic process at initial concentrations of Diclofenac of 10 mgL$^{-1}$. The positive values of $\Delta S^\circ$ showed the increased unpredictability of the solid/solution interface throughout the adsorption process.

\[ \Delta G^\circ = -RT \ln K_c = \Delta H^\circ - T \Delta S^\circ \]  
\[ \ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \]  
\[ \log K = \log A - (E_a/2.303RT) \]

**Table 3.1.9 (a,b) & Figure 3.1.9 (a,b): Thermodynamic parameters for the adsorption of Diclofenac**

<table>
<thead>
<tr>
<th>$\Delta G^\circ$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$\log_{10} K_c$</th>
<th>$1/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1147.92</td>
<td>26.806</td>
<td>76.58857</td>
<td>0.1978</td>
<td>0.003299</td>
</tr>
<tr>
<td>-1517.51</td>
<td>0.253135</td>
<td>0.003193</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2217.93</td>
<td>0.358525</td>
<td>0.003095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-2560.62</td>
<td>0.401495</td>
<td>0.003002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.1.9 (b)**

\begin{align*}
\text{Diclofenac} & \\
E_a & \text{Log } A & R^2 \\
\text{Fig. 3.1.9(a)} & \text{Fig. 3.1.9(b)} & \\
\text{Thermodynamic plot} & \text{Arrhenius plot} & \\
\end{align*}

FT-IR study

The Fig. 3.1.10 a and b display the ADCL samples’ FT-IR (NICOLET iS50, Thermo Scientific, USA) spectra both before and after adsorptions. Specifically the spectra offer evidence for the Boehm-declared presence of surface groups on the adsorbent's surface. The peak intensities between them differ substantially. The carbons have noticeable variations in almost every absorption band's intensity, which reflects how differently dense the respective
functional groups are. Some peaks in the adsorbate are lost after adsorption due to desorption, while a few peaks are slightly displaced to higher or lower wave numbers due to electrostatic forces. Adsorption confirmed that no new compounds were formed and that the peaks were not broadening, hence there are no new peaks. 

The surface of ADCL before adsorption is shown in Fig. 3.1.12a together with a few carbon flakes and different-sized micropores. Fig. 3.1.12b shows the surface of ADCL after adsorption with a significant number of pores and material debris filling the pores, in contrast to ADCL that has not been treated. Diclofenac molecules adhered to one another and interacted electrostatically to cause this. Even though the pores' surface area may have been reduced by the material debris clogging them, Diclofenac was still able to bind to and exchange ions with these sites. The surface morphology of ADCL was examined using scanning electron microscopy (SEM) both before and after adsorption. The relevant SEM micrographs are displayed in Fig. 3.1.12a and table 3.1.12b and were obtained using a JEOL JSM 6390 at a 20kV accelerating voltage. At such magnification, the ADCL particles showed rough areas of surface with clearly visible micropores.

XRD study
One of the microstructural examination techniques used to determine the crystallinity of an adsorbent is X-ray Diffraction analysis (XRD). The Diffraction of X-rays Utilizing an X-ray Diffractometer 40KV/30mA, Model XRD 6000 SHIMADZU from Rigaku Corporation, Japan, studies of the adsorbent ADCL were conducted both before and after Diclofenac adsorption. Fig. 3.1.11a and Fig. 3.1.11b depict the diffraction patterns. The figures clearly show that there is no discernible difference between the adsorbent's spectra before and after adsorption. This might be as a result of the fact that adsorption does not change the chemical composition of the adsorbent's surface. Weak Van der Waals forces control the adsorption, which is a physical process.

SEM
A scanning electron microscope was used to look at the adsorbent's surface (SEM). The exact surface characteristics of the adsorbent are shown in the SEM figure.
CONCLUSION

The adsorption characteristics studies on the removal of therapeutic drug Diclofenac on the acid digested carbon of waste leather were analysed by varying the physico-chemical conditions. The minimum particle size gives maximum number of surface area and adsorbed more, 92.43% for 0-63 micron. Acid pH ranges were optable for the adsorption of Diclofenac on this ADCL. But different adsorbate preferred different acidic pH range of pH from 1–6. In the basic pH range the adsorption is very pure due to the formation of the hydroxide precipitate. In this case at pH 5, 92.15% of adsorption takes place. The percentage of adsorption of Diclofenac is directly proportional to the adsorbent dosage and contact time and inversely proportional to the initial concentration of the adsorbate. Were found out from this study. Order of this adsorption is pseudo second order kinetics and it belongs to the physisorption, because of no chemical bond formation between the adsorbent and adsorbate. For these investigations, the freundlich and Langmuir isotherm model is appropriate. The thermodynamic analysis shows negative $\Delta G^0$, positive $\Delta H^0$, and $\Delta S^0$ values, indicating that this adsorption is, respectively, spontaneous, feasible, and physical in origin. The spectral evidence from the FT-IR, SEM, and XRD is in support of the aforementioned empirical evidences and provided the strong applicability on the removal of therapeutic drug Diclofenac pollution from water bodies as well as from industrial effluence. This is the cheapest and most ecologically responsible way to remedy water contamination.

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REFERENCES


