Evaluation of the Efficiency of Hydrochloric Acid Modified Red Mud in Removing Diclofenac from Aqueous Solution

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Abstract: This study is aimed at evaluating the efficiency of hydrochloric acid, modified red mud in removing diclofenac (DCF) from aqueous solution. Red mud produced was treated with 2.25 M HCl, noted RMH. Batch experiments were used to determine the effects of time of stirring/initial concentration, pH, adsorbent dose and temperature on the efficiency of DCF adsorption on RMH. pH was the main parameter that controls DCF adsorption, with removal of 95 % at pH of 4 in 10 minutes. But the increase in temperature decreased DCF adsorption from 95 % at 298 K to 62 % at 333 K. Equilibrium was attained in 10 minutes for all the parameters tested. Langmuir isotherm fitted the adsorption with maximum adsorption capacity values of 500 and 222 mg/g at 1050 and 500 mg/L initial concentrations respectively. Adsorption was very favourable with very low R_L values (0.003-0.0003). Adsorption energies obtained from the Dubinin–Radushkevich isotherm revealed that physical adsorption was the main mechanism of adsorption. Pseudo-second order kinetic model best explained the adsorption with initial sorption rates increasing with increasing initial concentration. The removal process was very spontaneous and exothermic. HCl treated red mud is very efficient in removing DCF from aqueous solution.
Keywords: Adsorption, Diclofenac, pH, Red mud, Thermodynamics.

1 Introduction

The world population currently stands at about six billion people and is expected to reach eight billion within a generation [1, 2]. This increasing trend in the world population directly implies an increase in different human and industrial activities. The consequences of these activities are the pollution of the environment, particularly surface and subsurface waters with different products from these activities. One group of such products are the Pharmaceutical products described as being amongst the group of emerging contaminants in the world and particularly in aquatic environments [3, 4]**.** They include a wide range of different types of chemical substances which include prescription and over the counter therapeutic drugs, veterinary drugs, fragrances, cosmetics, sunscreen products, diagnostic agents, and nutraceuticals [4]. These products enter the environment through various sources such as human activities through direct discarding of unused medication, effluents from pharmaceutical manufacturing plants, use of drugs by human and veterinary, excretions from humans as unchanged compounds, metabolites or conjugates via urine and feces and wastewater treatment plants as they are not eliminated in wastewater treatment plants [3, 5]. They are a serious threat to both humans and the environment because of their polar, water solubility, persistence and microbial resistance properties, and their ability to bioaccumulate in the food chain [5].

One of the most studied pharmaceutical products is Diclofenac (DCF), a non-steroidal anti-inflammatory drug which has potential toxic effects on no-target organisms [5]. Worldwide consumption of DCF amounts to 940 tons per year [5]. It has been detected in effluents in a many countries [4-6] as its removal during wastewater treatment processes typically ranges from 21 to 40 % [5, 7]. This justifies their presence in surface water, groundwater and even in drinking water at very low concentration. Author [5] has reviewed the toxic effects of DCF, some of which include death of birds shortly after scavenging on contaminated livestock in India and Pakistan; endocrine disruption and reducing hatching success of fish eggs as well as damage of their digestive organs. It also causes oxidative stress and reduced testosterone level that can have a negative impact in aquatic organisms.

The general treatment methods of pharmaceuticals wastewater are physicochemical and conventional biological processes [8] but the biological processes have been proven to be inadequate due largely to the complex molecular structure of pharmaceuticals [9, 10]. Physico-chemical processes such chlorination and use of activated carbon has been able to remove over 90 %, but chlorination produces chlorine as a by-product [4, 11]. But the high cost of production and of regeneration of activated carbon limits its use and encourage its substitution by low cost materials. One of such low cost material is red mud (particularly, in Cameroon which host the 6th world bauxite reserves [12, 13], a toxic waste product of the Bayer process for the production of alumina from bauxite. 150 million tons of this residue are produced annually worldwide as approximately, 1.0–2.0 tons of toxic red mud (pH 10-13) are generated per ton of alumina produced [14]. Unfortunately, current estimates show that only about 2-4.5 tons are used annually in some way including its use as adsorbent [14]. There is the need therefore to encourage the use of red mud as adsorbent as this will provide an alternative to disposal with its environmental consequences.

Red mud has been largely used as adsorbent in wastewater treatment for removal of metal ions, dyes, phenolic compounds and inorganic anions as presented in the following reviews [15-18]. However, none of these reviews and other literature has studied the use of red mud for the removal of DCF from aqueous solution. This work therefore involves the removal of diclofenac (DCF) from aqueous solution using hydrochloric acid activated red mud as studies on the use of red mud for DCF removal are scarce in literature. Results will not only enhanced red mud valorization but also improve the economy of DCF removal, hence reducing environmental pollution and improving water quality.

2 Experimental Section

2.1 Preparation of adsorbent

The red mud used for this study was produced in our laboratory from bauxite collected at Minim-Martap bauxite deposit [19] as described in [20]. Acid activation of red mud was then carried out as described by [21] in which 10 g of water-washed and dried red mud, was boiled in 200 mL of 2.25M HCl concentration for 20 minutes. The acid slurry was then filtered on a Whatman filter paper N^0 1, the residue washed with distilled water and dried at 40 °C (to avoid degradation of structure). Acid modification improves the adsorbent specific surface area, pore structure and surface chemical functional groups. This acid modified red mud was designated as RMH. It was used for adsorption studies without further treatment. It has a pH of 2.12 with the major elements being SiO_2 (2.21%), Al_2O_3

(16.10 %), Fe_2O_3 (52.29 %), TiO_2 (5.79 %). It also contain 67.50 % mesopores, 30 % macropores and 2.5 % micropores with a BET surface area of 23.80 m^2/g, total pore volume of 0.109 cm^3/g and average pore width of 18.38 nm [21].

2.2 Adsorption experiments

A 1050 mg/L DCF stock solution used for adsorption study was prepared by dissolving 14 Diclofenac 75 mg tablets (each tablet contains 75 mg of DCF) manufactured by Jiangxi Xierkangtai pharmaceutical co. Ltd in 1 liter of distilled water. DCF is soluble in water because it is a sodium salt {2-[(2, 6-dichlorophenyl) amino] benzene acetic acid, sodium salt} with a molecular formula of $C_{14}H_{11}Cl_2NO_2$, molecular weight of 298.15 g/mole, log K_{ow} of 0.7-4.15 and pKa value of 4.15 [3, 22]. A 500 mg/L of DCF working solution was also prepared by diluting the 1050 mg/L stock solution. Kinetic studies were performed using concentrations of 1050 mg/L and 500 mg/L while the influence of pH, adsorbent dose and temperature were carried out using the concentration of 500 mg/L. Modeling of the kinetics and isotherms of adsorption was done using the data obtained from the kinetic studies. All the adsorption studies were carried out at a pH of 4 (except for the influence of pH), a temperature of 298 K (except for the influence of temperature) and 0.2 g of RMH (except for the influence of adsorbent dose following our preliminary test. All DCF initial solution pH was adjusted using 0.1M HCl or NaOH. Batch experiments were performed in 250-mL stoppered Erlenmeyer flasks with 100 mL of working solution. For kinetic studies, five separate 250-mL stoppered Erlenmeyer flasks, each containing 100 mL of either 1050 mg/L or 500 mg/L DCF solution and 0.2 g of RMH were stirred at 100 rpm respectively for 5, 10, 20 40 and 60 minutes and allowed for 4 hours to decant. The influence of pH was studied by varying pH of solution from 2 to 10 at an initial DCF concentration of 500 mg/L, stirring time of 10 minutes, 0.2 g of RMH and decantation time of 4 hours. Equally, the effect of temperature was performed at identical initial concentration and stirring time for temperatures of 298 K, 303 K, 313 K and 333 K while the influence of adsorbent dose was carried out by varying the amount of RMH from 0.05 to 0.3 g. After 4 hours for solution to decant in each case, 5 mL of the solution was obtained by decantation and the residual amount of DCF was determined using a UV-Visible spectrophotometer (Spectro 23 RS, LaboMed.inc.) at a wavelength of 436 nm. The spectrophotometer was calibrated for DCF ≤ 90 mg/L ($R^2 = 0.9961$).

The amount of DCF adsorbed at time 't' was computed according to the following equation:

$$q_e = \frac{(Co - Ce)V}{m} \qquad (1)$$

where q_e is the adsorption capacity at time 't' (mg/g), C_0 is the initial DCF concentration (mg/L), Ce is the DCF

residual concentration (mg/L) at time t, 'm' is the adsorbent weight (g) and V is the volume of the DCF solution (L).

Percentage removal of DCF was calculated as:

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} x\ 100 \quad (2)$$

3 Results and Discussion

3.1 Effect of stirring time and initial concentration

The results of the influence of stirring time on the removal of DCF by RMH at two different initial concentrations are shown in figure 1. The adsorption of DCF on RMH takes place rapidly in the first 5 minutes of stirring with the removal of more than 99 % (520 mg/g) for initial concentration of 1050 mg/L and 92 % (230.43 mg/g) for 500 mg/L. The fast adsorptions at the initial stage indicate higher driving forces that make fast transfer of DCF to the surface of RMH with many free sites available. However, equilibrium is established in 10 minutes for the two initial concentrations; 96 % (506.14 mg/g) for 1050 mg/L and 95 % (239 mg/g) for 500 mg/L. The decrease from 99 to 96 % at equilibrium for 1050 mg/L and an increase from 92 to 95 % for 500 mg/L are due to the fact that, at lower concentration, the ratio of initial number of DCF to the available sorption sites is low and subsequently the fractional adsorption becomes independent of the initial concentration. At higher concentrations, however, the available sites of adsorption become fewer or there is saturation of the available active sites of the surface functional groups, thus preventing further DCF uptake. Generally, adsorption in solution involves four steps: diffusion from solution, migration to the surface, diffusion into the pores and adsorption. Thus, fast attainment of equilibrium (or steep gradient) indicates the mechanism of adsorption of DCF on RMH surface is governed by adsorption step, indicating strong affinity of DCF for RMH surface. These results are better than those of [23] for removal of DCF on Cyclamen persicum tubers based activated carbon with 70-72 % removal in 120-150 minutes.
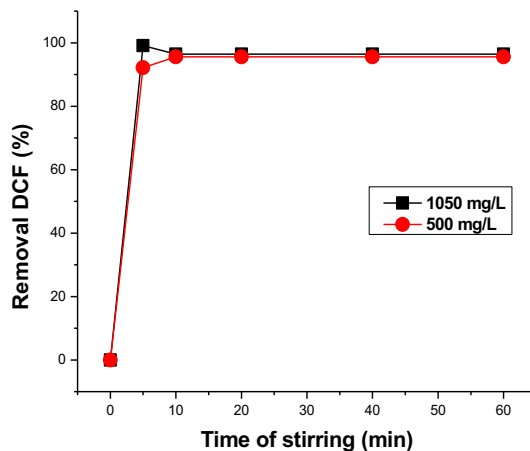

Figure 1. Effect of stirring time at two initial concentrations (temperature, 298 K; adsorbent, 0.2 g/L; solution pH, 4) on DCF removal by RMH.

3.2 Effect of DCF solution pH

The pH of the solution is an important factor in the adsorption process as most geochemist describes the pH as the master variable, because most reactions are partial functions of pH and therefore changing the pH can drive the reaction forward or backward [24]. The effect of DCF solution pH on its removal by RMH is given in figure 2, where it is observed that DCF removal is more favourable in the acidic region; 65 % at pH of 2 with maximum removal occurring at a pH of 4 (95 %). Contrary, very low removal is observed at pH of 7 (3.6 %), 33 and 26 % at pH of 8 and 10 respectively. According to [25] and [26], the adsorption of pharmaceuticals with acidic character ((clofibric acid, DCF, ibuprofen, ketoprofen and naproxen)) at pH greater than the pKa (pKa of DCF is 4.15) results in both the adsorbent and the adsorbate having negatively charged surfaces. Thus, resulting in electrostatic repulsion that hinders the adsorption and making the process more reversible. However, the optimal adsorption of DCF at pH of 4 (almost equal to pKa), is probably because DCF is in anionic form at this pH, thus interacting strongly with the positively charged adsorbent surface through electrostatic forces. Authors [27] and [23] also obtained optimum DCF adsorption on activated carbon at pH of 4.1 and 2 respectively.
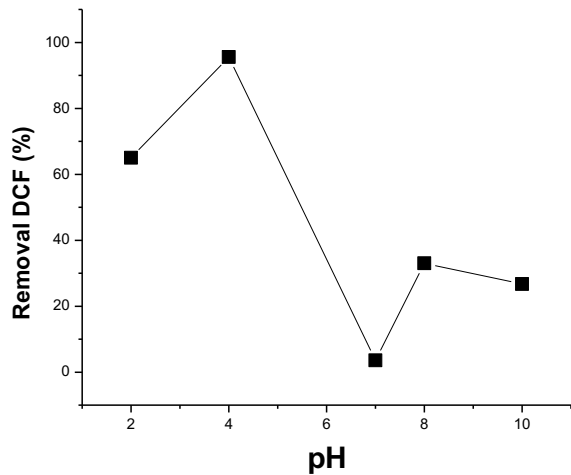
Figure 2. Effect of pH (Co, 500mg/L; stirring time, 10 minutes; temperature, 298 K; adsorbent, 0.2 g/L) on DCF removal by RMH.

3.3 Effect of adsorbent dose

The effect of adsorbent dose of DCF removal on RMH is shown in figure 3. The percent of DCF removal increased by increasing dosage of RMH up to 0.2g (optimum dose), after which an increase to 0.3 g was not effective, reducing percentage removal from optimum value of 95 % at 0.2 g to 85 %. At a higher adsorbent dosage, there is a very fast adsorption onto the adsorbent surface, which results in a lower adsorbate concentration in the solution, leaving many adsorption sites on the adsorbent surface unsaturated [28]. However, the higher adsorbent dose creates particle aggregation, resulting in a decrease in the total surface area and an increase in diffusional path length both of which contribute to decrease in amount adsorbed [29].
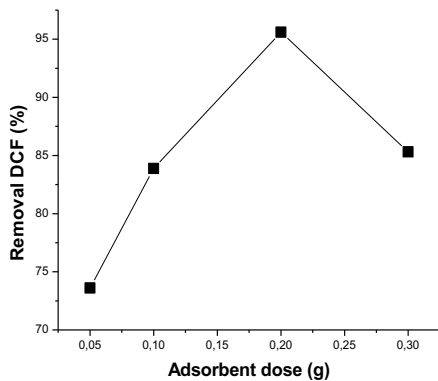

Figure 3. Effects of adsorbent dose (Co, 500mg/L; stirring time, 10 minutes; temperature, 298 K; solution pH, 4) on DCF removal by RMH.

3.4 Effect of DCF solution temperature

Increase in temperature showed a significant negative effect on DCF adsorption on RMH as presented in figure 4, decreasing the percentage removed from 95 % at 298 K to 62 % at 333 K. Similar results were obtained by [25] on the adsorption of naproxen and ketoprofen by carbon black. The decrease is thus attributed to the increase in the solubility of the pharmaceuticals (DCF in this case) with an increase in temperature, which affects its adsorption because it would have an increase affinity for the solvent compared to the adsorbent. Also, there is a decreased in the force of the attraction between the DCF and adsorbent because the increasing temperature caused an increase in the agitation of the dissolved chemical species, reducing its interaction with the adsorbent. The exothermic nature of the adsorption ($\Delta H°$ is -59.55 KJ/mol, Table 3) will also cause the decrease in removal percentage with increasing temperature because as heat is released to the system, the equilibrium shifts to the opposite direction of the reaction.
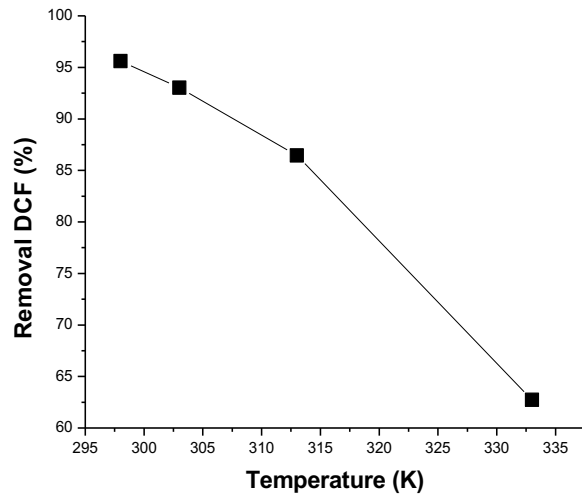

Figure 4. Effects of temperature (Co, 500mg/L; stirring time, 10 minutes; adsorbent, 0.2 g; solution pH, 4) on DCF removal by RMH

3.5 Modeling of adsorption Kinetics

Adsorption Kinetics of DCF studies are very important as they help in the understanding of the rate of adsorption and the rate-limiting step of the transport mechanism thus providing the basis for the modelling and design of the process [30]. Three different models are: Pseudo-first-order given (equation 3a), Pseudo-second-order (equation 3b) and Intraparticle diffusion (equation 3c) were used to model the adsorption kinetics.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3a)$$
$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (3b)$$
$$q_t = k_{id} t^{0.5} + C \qquad (3c)$$

Where q_t is adsorption capacity (mg/g) at time t (min), qe,

is the equilibrium adsorption capacity (mg/g), K_1 is the pseudo-first-order equilibrium rate constant (min^{-1}), k_2 $(g\mu mol^{-1}min^{-1})$ is the pseudo-second-order constant and k_{id} $(mg\ g^{-1}\ min^{1/2})$ is the rate constant of intraparticle diffusion and C is intercept. As observed from figure1, equilibrium was attained in10 minutes such that $ln(q_e - q_t)$ will be valid only for one point at 5 minutes, thus First-order modeling is not possible. For the process to be completely controlled by the intraparticle diffusion model, the plot of q_t versus $t^{0.5}$ yields a straight line passing through the origin with the slope giving the rate constant, k_{id}. The intraparticle diffusion model plot gave an identical R^2 of 0.3998 for 1050 and 500 mg/L with an intercept value C of 517.57 mg/g for 1050 mg/L and 232.14 mg/g for 500 mg/L. Intraparticle diffusion model therefore does not describe DCF adsorption on RMH, indicating the absence of diffusion of DCF into the pores of RMH. If the second-order kinetics is valid, then the plot of t/qt versus t should be linear. The initial adsorption rate, h (mg/g·min), as $t \rightarrow 0$ can be defined as $h = k_2 q_e^2$. The initial adsorption rate (h), the equilibrium adsorption capacity (q_e), and the second-order constant (k_2) can be determined experimentally from the slope and intercept of plot t/qt versus t, figure 5 and values of the parameters are shown in Table 1. It is seen from table 1 that experimental and calculated q_e values on RMH were well correlated for the two initial concentrations and the R^2 values for these two initial concentrations were all unity. However, the 1050 mg/L adsorption on RMH showed a higher initial sorption rate than the 500 mg/L initial concentration (table 1). The half adsorption time, $t_{1/2,}$ of DCF is the time required for RMH to uptake half the amount adsorbed at equilibrium and is often considered as a measure of the rate of adsorption and for the second-order process is given by [31]:

$t_{1/2} = 1/K_2q_e^2$ (4)

The determined values for $t_{1/2}$ are given in table 1. At 1050 mg/L DCF initial concentration, adsorption is 4 times faster than at 500 mg/L on RMH. Probably as the initial concentration of DCF increased, the driving force that caused it to interact with the active sites of RMH also increases [32]. Pseudo-second-order model represents a better fit for DCF adsorption on RMH at the two initial concentrations than the other tested models indicating a two-step process; migration of DCF molecules to the red mud surface followed by attachment.
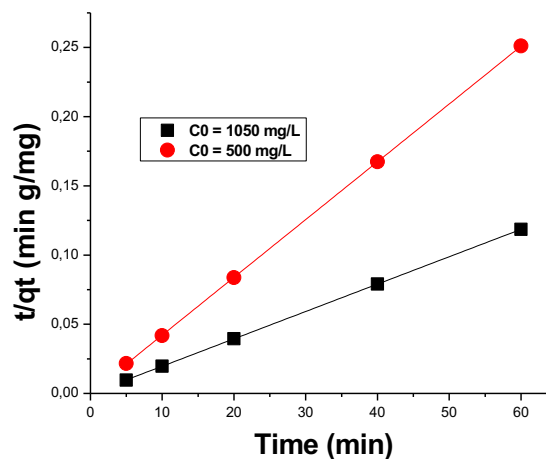

Figure 5. Pseudo-second order kinetic model plots of DCF adsorption on RMH

Table 1: Kinetic parameters for DCF removal by RMH

Models	Parameters	1050 mg/L	500 mg/L
Pseudo-second-order	k_2(g/mg/min)	0.040	0.044
	qe, cal (mg/g)	500	238.1
	qe, exp't (mg/g)	506	239
	R^2	1.000	1.000
	h(mg/g·min)	10000	2500
	$t_{1/2\ (min)}$	0.0001	0.0004

3.6 Modeling of adsorption Isotherms

The equilibrium of the adsorption process is necessary for the determination of adsorption capacity and the nature of adsorbate-adsorbent interactions and was evaluated applying the linearized equations of the Langmuir (equation 5a), Freundlich (equation 5b) and Dubinin–Radushkevich (D–R) models (equation 5c) [33].

$\frac{Ce}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right)Ce$ (5a)

$lnq_e = lnK_F + 1/nlnCe$ (5b)

$lnq_e = lnX_m - K\varepsilon^2$ (5c)

Where Ce is DCF equilibrium concentration (mg/L), qe is the equilibrium adsorption capacity (mg/g), qm represents the monolayer adsorption capacity (mg/g), b is the Langmuir isotherm constant (L/mg), K_F is the Freundlich constant $(mg/g)(L/mg)^{1/n,}$ and n is the Freundlich exponent (dimensionless) which defines the extent of linearity of the adsorption. Xm the adsorption capacity of the sorbent (mg g^{-1}), K is a constant related to the adsorption energy $(mol^2$

kJ^{-2}), R the gas constant (kJ K^{-1} mol^{-1}), and T is the temperature (K). The significance of applying D–R model is to determine apparent adsorption energy, E (kJ/mol) which is given by equation 10.

$$E = 1/\sqrt{2\,K} \qquad (6)$$

Separation factor, R_L, which is considered as a more reliable indicator of the adsorption is defined by equation11.

$$R_L = \frac{1}{1 + bC_0} \qquad (7)$$

With b (L/mg) being the Langmuir constant and C_0 (mg/L) is DCF initial concentration. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible adsorption [33]. Linearized plots of these three models on RMH are shown in figures. 6a, b and c while the calculated isotherm parameters are presented in table 2. It was observed from table 2 that the three models all had an identical correlation coefficient (unity). However, for Freundlich model n is greater than one for the two concentrations. By definition, the adsorption intensity, n, is less than unity [34]; implying Freundlich model does not describe well DCF adsorption on RMH. Also a very low adsorption capacity value is observed for the D-R model. Conversely, a very high monolayer capacity was observed in the Langmuir model at the two initial concentrations on RMH with very low R_L indicating very favourable DCF adsorption. The b value at 1050 mg/L initial concentration was five times greater than at 500 mg/L showing a more favourable DCF adsorption with increasing concentration. The Dubinin–Radushkevich constants were calculated and are also shown in table 2. The value of E at 1050 and 500 mg/L was found to be 0.474 and 1.491 KJ/mol, respectively. These values are all less than 8 kJ/mol, suggesting that physical forces dominated the sorption process because if E is between 8 and 16 kJ/mol, ion exchange is the main sorption process but if E is lower than 8 kJ/mol, physical sorption is the main sorption mechanism and if the value is greater than 16 kJ/mol, it may be chemisorption [33, 35]. The good fit of the Langmuir isotherm to a larger extent and Dubinin–Radushkevich isotherms to a lesser extent suggest DCF adsorption on RMH does not only occur on a dominated homogenous surface but on a mix homo-heterogenous RMH surface. The comparison of DCF adsorption on the red mud with other adsorbents (table 3), principally activated carbon shows that red mud activated with HCl is very efficient for DCF removal from aqueous solution.
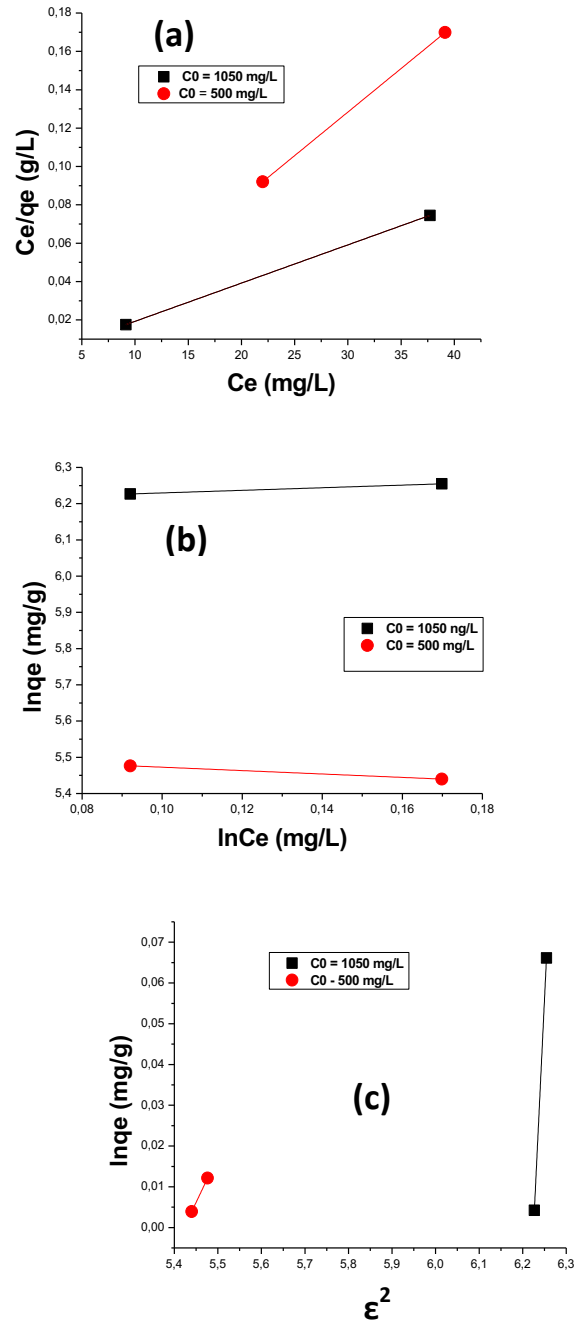
Figure 6. (a) Langmuir, **(b)** Freundlich and **(c)** Dubinine Radushkevich isotherms plots for DCF removal on RMH

Table 2: Isotherm parameters for DCF removal by RMH

Models	Parameters	1050 mg/L	500 mg/L
Langmuir	q_m (mg/g)	500	222.22
	b (L/mg)	2.857	0.577
	R^2	1.000	1.000
	R_L	0.0003	0.003
Freundlich	K_F (mg/g)(L/mg)$^{1/n}$	489.75	249.56
	n	2.796	2.131
	R^2	1.000	1.000
Dubinin Radushkevich	Xm (mg/g)	9,661E-07	0,295
	K (mol^2/KJ^2)	2.225	0.225
	E (kJ/mol)	0.474	1.491
	R^2	1.000	1.000

Table 3: Comparison of adsorption capacities of activated carbon with RMH for DCF removal

Adsorbent	Adsorption capacity (mg/g)	Reference
AC from Sabel grape bagasse	5.12-23.77	[5]
Functionalized silica based porous materials AC	5.89-40.55	[5]
Granular carbon nanotubes/alumina hybrid	190.52	[5]
Activated biochars	372	[5]
GAC and PAC	214 and 87.4	[5]
Trimethylsilylated mesoporous SBA-15 AC	156.35	[5]
Carbone Xerogels	32.4-40.2	[5]
Activated Carbon	103	[6]
Acid activated red mud	**500-222**	**This study**

AC = activated carbon

3.7 Determination of thermodynamic parameters
For adsorption thermodynamics studies, the changes in Gibbs free energy (G*)*, enthalpy (H), and entropy (S) for the adsorption process were obtained using the equations 8a and 8b [36]:

$\Delta G = -RT\ln K$ (8a)

$\ln K = (\Delta S/R) - (\Delta H/RT)$ (8b)

Where *R* is the ideal gas constant (kJ mol^{-1} K^{-1}) and *T* is the temperature (K). The enthalpy change (H) and the entropy change (S) are calculated from a plot of lnK versus 1/T.

K was calculated from K = C$_{ads}$/C$_e$ (8c)

C$_{ads}$ = C$_o$ - C$_e$ (8d)

Where K is the equilibrium constant, C$_e$ is the concentration of DCF in solution at equilibrium (mg/L) at temperature T, C$_o$ is the initial DCF concentration (mg/L), C$_{ads}$ is the concentration of DCF in the adsorbent at equilibrium (mg/L) at temperature T.

Table 4 present results of calculated thermodynamic parameters. The negative value for the Gibbs free energy shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction decreases with increasing temperature. These values ranged from -1.44 to -7.62 KJ/mol indicating a principally physical adsorption because the Gibbs free energy values from 0 to 20 kJ/mol and 80 to 400 kJ/mol represent physical and chemical adsorption respectively [37-38]. The negative value of ΔH^0 indicates that the adsorption is an exothermic process. Implying there will be a decrease in adsorption capacity with increase in temperature. There is a reduction in the disorderliness at solid-liquid interface as DCF is adsorbed on the RMH surface as indicated by the negative value of entropy change. This, according to [39] probably originated from the formation of more than one layer of adsorption, which would organize the system and hence reduce the randomness.

Table 4: Thermodynamic parameters for DCF removal by RMH

C$_0$ (mg/L)	Temperature (K)	Equilibrium constant	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol K)
C$_0$ = 500	298	21.73	-7.62	-59.55	- 0.175
	303	13.34	-6.53		
	313	6.38	-4.82		
	333	1.68	-1.44		

C$_0$ = initial diclofenac concentration

4 Conclusions

The efficiency of red mud modified with hydrochloric acid in the removal of diclofenac from aqueous solution was tested. The modified red mud was very efficient in removing DCF from aqueous. This process was principally controlled by the pH of DCF solution, with optimum adsorption occurring at pH of 4. Increased in initial concentration had no effect on the time taken to reach equilibrium which was ten minutes for all the concentrations used. However, increased in temperature had a very negative effect on DCF adsorption on RMH reducing the percent removal from 95 % at 298 K to 62 % at 333 K. Langmuir isotherm model best fitted the process as compared to other tested models with a maximum monolayer capacity of 222-500 mg/L. Adsorption of DCF

on RMH was very favourable with the dimensionless parameter R_L of 0.003-0.0003. The adsorption of DCF on RMH occurred by physical adsorption as indicated by energy obtained from Dubinin–Radushkevich modeling. Pseudo-second order kinetic model best described the adsorption of DCF on RMH with a high correlation coefficient and strong agreement between calculated and equilibrium amounts adsorbed. Increased in the initial concentration increased the initial adsorption rate by 4 times. DCF removal on RMH was spontaneous and exothermic, with the highest removal occurring at room temperature.

Red mud is an inexpensive and readily available material and showed higher adsorption of DCF from aqueous solution compared to activated carbon (Table 4), which has up to date been the best material to remove DCF from aqueous solution [4]. Thus, HCl modified red mud can effectively find applications in industries such as pharmaceuticals for the removal of DCF from its effluents.

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