Adsorption of Caffeine and Ciprofloxacin onto Pyrolitically Derived Water Hyacinth Biochar: Isothermal, Kinetic and Thermodynamic Studies

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Abstract: In this work, the adsorptive features of water hyacinth (*Eichhornia crassipes*) derived biochar for sequestration of ciprofloxacin and caffeine from aqueous solution is reported. The isothermal behaviour, adsorption kinetics, mechanisms and thermodynamic parameters were investigated in batch mode. Langmuir and Freundlich models described the equilibrium adsorption data with regression values > 0.9. The kineticsdata obeyed the pseudo-second-order kinetic law while intraparticle pore diffusion was not the only rate controlling step. The computed thermodynamic parameters, namely change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) indicated that the adsorption processes were spontaneous and exothermic with less randomness. pH dependence studies depicted multi-mechanistic adsorption for both compounds and is hypothesized to involve hydrophobic interactions besides other non-coulombic interactions. The findings demonstrate that water hyacinth biochar presents an excellent low cost and environmentally benign adsorbent for mitigation of pharmaceuticals from water with a removal efficiency of above 60 % for caffeine and ciprofloxacin.

Key words: Adsorption, ciprofloxacin, caffeine, biochar, water hyacinth.

1. Introduction

PhCs (pharmaceutical compounds) are compounds manufactured for use in health care as medicinal drugs to prevent, diagnose, mitigate or cure diseases in humans as well as animals [1]. PhCs have been frequently detected in surface waters, treated WWs (wastewaters) and in drinking portable waters [2-4]. Their occurrence in water and exposure to non-target organisms has been associated with chronic toxicity, endocrine disruption, development of bacteria resistantstrains and congenital anomalies [5]. Conventional WWTPs (wastewater treatment plants) are not designed to effectively remove these pollutants. As such, alternative water treatment approaches are still critically needed. Adsorption process is the widely used method for PhC removal

from water since it is eco-friendly, cost effective and relatively simple. In recent years, agricultural feedstock based biochars have received much attention among researchers due to biomass abundance exceeding alternative use [6]. Water hyacinth (*Eichhornia crassipes*), a floating aquatic plant, is an abundant bio-resource, which can be harnessed in remediation of WWs. It is found in the Lake Victoria region of Kenya and is considered an environmental and economic menace [7-8]. It is described as one of the most high yielding plant, with 10 plants yielding up to 600,000 more within an 8-month growing period and completely covering upto 0.4 ha (1 acre) of a natural freshwater surface [7]. In the present work, water hyacinth biomass is used as a precursor for development of residue-derived biochar for removal of caffeine (1-cyclopropyl-6-fluoro-4-oxo-7-(piperazin-1-yl)-quinoline-3-carboxylic acid) (CAF) (a central nervous stimulant) and

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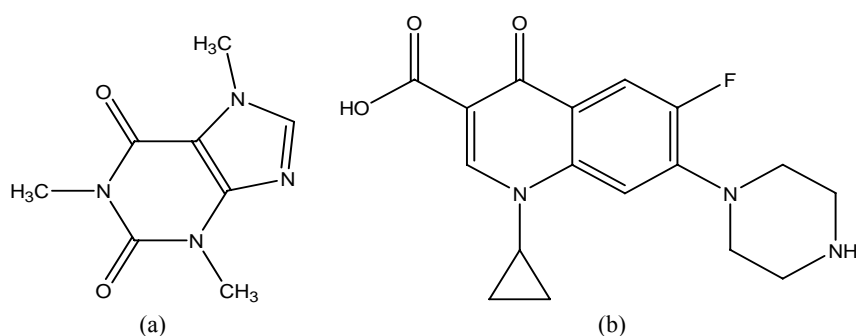(a)   (b)

Fig. 1   Structures of caffeine (a) and ciprofloxacin (b).

Table 1   The physico-chemical parameters of CIP and CAF.

Physico-chemical parameters	CAF	CIP
Molecular weight	194.19 g·mol^{-1}	331.34 g·mol^{-1}
Molecular formulae	$C_8H_{10}N_4O_2$	$C_{17}H_{18}FN_3O_3$
pK$_a$	14 (25 °C)	6.1-8.7
Log K$_{ow}$	-0.07	0.28 (non-ionized)
Water solubilty	21,600 (mg·L^{-1})	150 (mg·L^{-1})

[Adopted from 4, 9]

ciprofloxacin (1,3,7-Trimethylpurine-2,6-dione) (CIP) (an antibacterial agent) (Fig. 1)from aqueous solutions, as model PhCs. Their physico-chemical parameters are represented in Table 1.

2. Materials and Methods

2.1 Procedure

2.1.1 Preparation of Adsorbent

Eichhornia Crassipes was collected from Lake Victoria, Kenya. The roots of the plant were chopped into pieces. They were then washed with de-ionized water to remove all the dirt and air dried under a shade. Preparation of biochar was done through slow-pyrolysis at 350 °C and at a heating rate of 10 °C minute^{-1} and a dwell time of 60 minutes using a furnace. The sample was again washed with de-ionized water until the effluent from it was neutral to litmus and oven-dried at 100 °C for 2 h. FTNIR (Brucker model) studies indicated the carbon content to be 9.1%; ash content was 8.2% while the moisture content was 6.4%.

2.2.2 Effect of Contact Time

The adsorption kinetic experiments were performed by batch technique separately and in triplicate for CAF and CIP PhCs. A mass of 0.1 g of the WHB (water hyacinth biochar) was dispersed into a 250 mL conical glass flask containing 50 mL of a 5 mg·L^{-1} PhC compound at 298 K and agitated at 120 rpm using an overhead temperature-controlledshaker (GFL-3006). At pre-determined regular time intervals, residual CAF and CIP in solution were determined by UV-VIS spectrophotometer (Shimadzu-1800 model) at 273 nm and 274.8 nm, respectively. The amount of PhC adsorbed per unit mass at time (t) was calculated as:

$$qt = \frac{(C_o - C_e)V}{M} \qquad (1)$$

where, C_o and C_e are the initial and equilibrium concentration (mg·L^{-1}), M is the mass of the adsorbent (g) and $V$is the volume of the solution (L). To obtain the kinetic parameters, the kinetic data were fitted to two widely used kinetic models, namely, pseudo-second-order, [10] and intra-particle diffusion, Ref. [11] models represented in the equations below:

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \qquad (2)$$

Intraparticle diffusion model:

$$q_t = K_p t^{0.5} + C \qquad (3)$$

where, t (mins) and q_t (mg·g^{-1}) are time and amount adsorbed at equilibrium time, respectively while q_e (mg·g^{-1}) is the equilibrium adsorption capacity. K_2 and K_p are rate constants.

2.2.3 Adsorption Isotherm Studies

To generate the adsorption isotherms, 0.1 g WHB were separately, in triplicate vessels dispersed into 50 mL of CAF and CIP solutions with varying concentrations ranging from 2 to10 mg·L^{-1} at 298 K. After equilibration, the residual PhC in solution was analyzed and the equilibrium adsorption capacity, q_e at different initial adsorbate concentration was obtained by the Eq. (4):

$$qe = \frac{(C_o - C_e)V}{M} \qquad (4)$$

The experimental data were then fitted to linearized Langmuir and Freundlich isotherm equations (Table 2).

where, q_e (mg·g^{-1}) and C_e (mg·L^{-1}) are the solute uptake and thesolution concentration at equilibrium, respectively andQ_o (mg·g^{-1}) is the monolayer adsorption capacity. C_o (mg·L^{-1}) and R_L are the initial solution concentration and Langmuir separation constant, respectively. The K_L and K_f are the Langmuir and Freundlich constantsand 1/n is related to the adsorption affinity or surface heterogeneity [15].

2.2.4 Thermodynamic Studies

The effect of temperature changes on the adsorption was studied in the range 298-338 K. Here, 0.1 g of WHB was separately dispersed into 50 mL of 5 mg·L^{-1} of CAF and CIP and the contentsshakenat different temperatures (298, 308, 318, 328 and 338 K), all in triplicate, until equilibration. The thermodynamic parameter ΔG was estimated using the following equations:

$$\Delta G = -RT \ln k_c \qquad (5)$$

$$K_c = \frac{C_{ads}}{C_e} \qquad (6)$$

where, K_c is the equilibrium constant, C_e is the equilibrium concentration in the solution (mg·L^{-1}) and C_{ads} is the equilibrium solid phase concentration (mg·L^{-1}). The ΔH and ΔS were obtained from slope and intercept of the Van't Hoff plot (Eq. (7)), respectively. [16, 17]

$$\ln K_c = \frac{\Delta s}{R} - \frac{\Delta H}{R}\frac{1}{T} \qquad (7)$$

2.2.5 Effect of pH

The pH at point of zero surface charge (pH$_{pzc}$) is an important parameter that predicts the adsorbent's surface charge. In the present study, the WHB's pH$_{pzc}$ was determined using the standard protocol reported in literature [18]. The effect of pH on the amount of CIP and CAF removal was analyzed over a pH range of 2 to 12. Briefly, 50 mL (5 mg·L^{-1}) of each PhC and 0.1 g biochar was placed in stopper glass conical flask and the pH adjusted using 1 M HCl and 1 M NaOH solutions. The solution was then agitated at120 rpm at 298 K until equilibration. The pH was measured using a pH meter (MrC 86505, scientific instrument).

Table 2   The Isotherm models.

Isotherm model	Equation	Parameters	Reference
Langmuir	$\dfrac{1}{q_e} = \dfrac{1}{Q_o} + \dfrac{1}{Q_o K_L C_e}$ $R_L = \dfrac{1}{1 + K_L C_o}$	Q_o (mg·g^{-1}), K_L (L·g^{-1}) R_L	[12] [13]
Freudlich	$\log q_e = \log K_f + \dfrac{1}{n}\log C_e$	K_f, n	[14]

2.2.6 Variation of Adsorbent Dosage

The effect of WHB dose on PhC removal was obtained by contacting 50 mL of 5 mg·L^{-1} of the PhC with different weighed amount (0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g) of the WHB at 25 °C until equilibration.

3. Results and Discussion

3.1 Adsorption Kinetics

The adsorption dynamics of CIP and CAF onto WHB measured as a function of time depicted an instantaneous adsorption within the first 5 mins with 61.2 and 77.2% of CAF and CIP removed, respectively. This was then followed by a slower plateau-shaped phase implying pseudo-equilibrium condition with insignificant further adsorption (Fig. 2). The initial faster uptake of the PhCs is due to the large number of bare binding sites. Eventually, CIP had 80.4% being adsorbed while CAF had 76.4 %.

The kinetic data were fitted to pseudo-second-order kinetic model (Fig. 3) widely used to describe adsorption reactions onto biochars [15]. The high R^2 valuesclosest tounity (> 0.99) and convergence of the experimental adsorption capacities (q_{exp}) and the theoretical values (q_{cal}) (Table 3) indicate that the adsorption closely followed pseudo-second-order kineticsimplying the underlying assumptions of the model, namely, a chemisorption rate determining step and the reaction rate being proportional to the number of active binding sites on the adsorbent surface, possibly hold.

The initial adsorption rates (S$_{rate}$) and adsorption half lives (t$_{½}$) were generated from the regression plot in Fig. 3 using Eqs. (8 and 9), respectively.

$$S_{rate} = K_2 q_e^2 \tag{8}$$

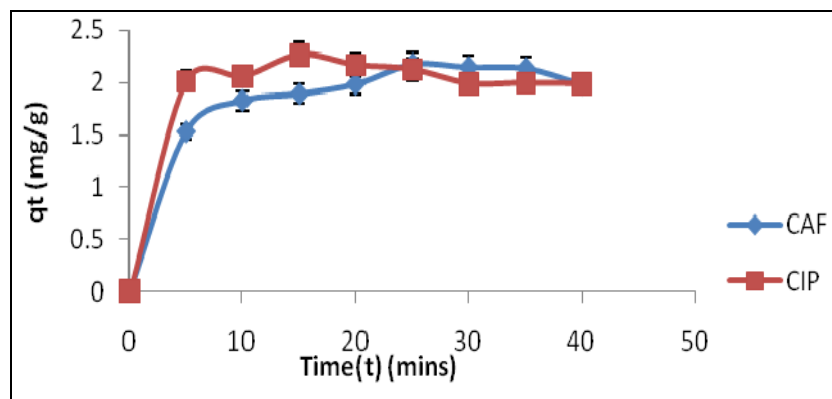$$t_{\frac{1}{2}} = \frac{1}{K_2 q_e} \tag{9}$$

Fig. 2   Variation of amount of CAF and CIP adsorbed onto WHB with contact time.
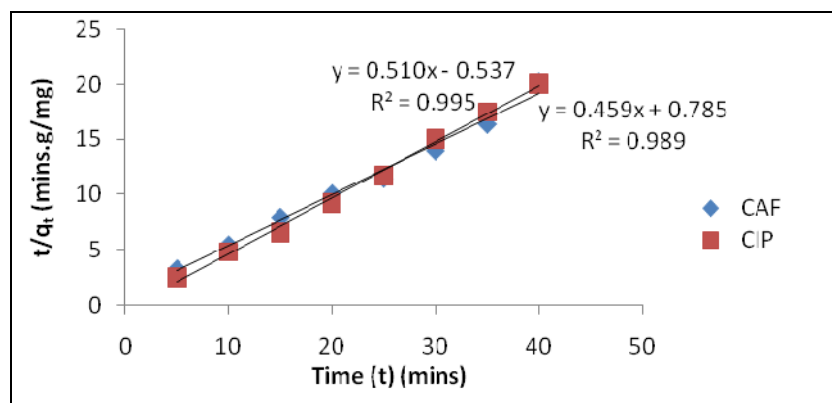

Fig. 3   Pseudo-second-order kinetics model graph for adsorption of CAF and CIP onto WHB.

Table 3 Pseudo-second-order kinetic parameters for CAF and CIP adsorption onto WHB.

PhC	R^2	Initial sorption rate(mg/g/min)	Adsorption half-life(mins)	K_2	q_e (cal)	q_e (Exp)
CAF	0.999	1.391	1.429	0.352	1.988	1.9126
CIP	0.998	2.817	1.439	-0.736	1.957	2.041

The adsorption rate of CIP (2.817) was faster than CAF (1.391) and the adsorption half life of CIP (1.439) was almost equivalent to that of CAF (1.429) (Table 3) which corroborates with the faster adsorption of CIP observed in Fig. 2. Among other parameters, adsorption process is affected by the solubility of the molecule. If high, it hinders the affinity of the molecule towards the carbon surface. In this sense, the slower adsorption process of CAF is possibly related to its higher solubility (21,600 mg·L^{-1}) when compared to that of CIP (150 mg·L^{-1}) (Table 1). Because of this hydrophilic nature, CAF has more affinity to the water molecule than to the adsorbent's surface [19]. Eventually, the amount adsorbed for both PhCs are almost equivalent. This can be attributed to the fact that CAF is a smaller molecule than CIP (Fig. 1) and therefore has a more efficient packing on the surface of the adsorbent [15].

The movement mechanism of the adsorbate molecules from the bulk solution to the adsorbent surface is reported to occur in multiple steps, such as; external surface diffusion, pore diffusion and adsorption on the pore surface [16]. The kinetic data were fitted to intraparticle diffusion model (Eq. (3)) in order to investigate the rate controlling step.

From the model, if the regression of pre-equilibrium q_t versus $t^{0.5}$ is multi-linear, as in Fig. 4, then several mechanisms influence the sorption behaviour. The low linear dependency on $t^{0.5}$ especially for CIP testifies that the adsorption dynamics of the PhCs studied onto WHB seem to be very weakly influenced by intraparticle diffusion mechanism. The plots also did not pass through the origin, implying that intraparticle diffusion is not the only rate controlling step. The straight lines had significant intercepts of 1.441 and 2.073 mg·g^{-1} for CAF and CIP, respectively, possibly due to the wide distribution of pore sizes of the biochar investigated [20].

3.2 Adsorption Isotherm Modeling

The distribution of the adsorbates between the aqueous and solid phases was evaluated by fitting the equilibrium data to Freundlich and Langmuir isotherm models. The generated isotherm parameters and corresponding R^2 values are shown in Table 4.

The experimental data fairly fitted both the Freudlich and Langmuir isotherms models for both compounds. Conformity to both models bespeaks of the heterogeneous nature of the WHB surface and corroborates the hypothesized multi-mechanistic nature of CIP and CAF adsorption process; consistent
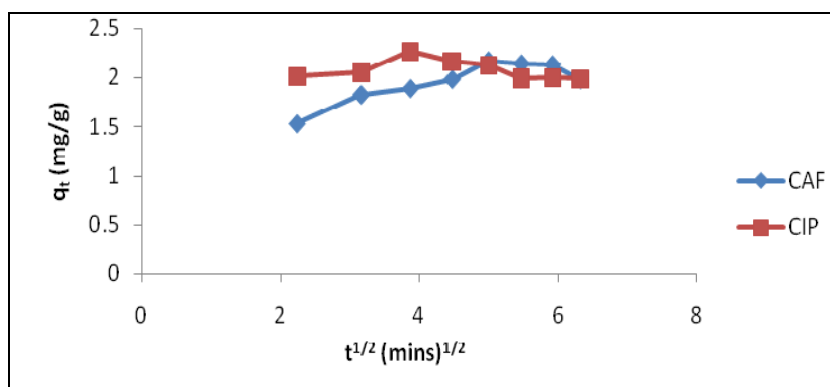

Fig. 4 Intraparticle diffusion model for CAF and CIP adsorption onto WHB.

Table 4 Adsorption isotherm parameters.

Isotherm model	Calculated parameter for CIP adsorption onto WHB	Calculated parameter for CAF adsorption onto WHB
Freundlich	$R^2 = 0.990$	$R^2 = 0.990$
	$n = 2.469$	$n = 2.101$
	$K_f = 1.422$	$K_f = 1.064$
Langmuir	$R^2 = 0.991$	$R^2 = 0.965$
	$Q_0 = 2.717$	$Q_0 = 2.488$
	$K_L = 1.460$	$K_L = 0.901$
	$R_L = 0.064$	$R_L = 0.0999$

Table 5 Thermodynamic parameters for CAF and CIP adsorption onto WHB.

Compound	Temp.(K)	% removal	$\Delta G(J \cdot mol^{-1})$	$\Delta H(KJ \cdot mol^{-1})$	$\Delta S(J \cdot mol^{-1})$
CAF	298	86.05	-4,503.80		
	308	81.05	-3,720.86		
	318	70.70	-2,329.10	-31.402	-90.45
	328	63.75	-1,540.06		
	338	59.75	-1,110.51		
CIP	298	86.42	-4,584.93		
	308	79.30	-3,439.12		
	318	73.28	-2,667.22	-26.754	-7.51
	328	69.39	-2,231.64		
	338	62.78	-1,469.34		

with the kinetics results earlier discussed. The implied heterogeneity of WHB surface was confirmed by the Freundlich constant, 1/n, which lies between 0 and 1 for heterogeneous surfaces. Furthermore, with n being more than 1, then the adsorption is a physical process and the values of n which lies within the range of 1–10 represent good adsorption [13, 21]. Moreover, the K_f and n values for CIP are relatively slightly higher than for CAF suggesting a higher affinity of CIP for the sorbent sites. This is consistently evidenced by the theoretical Langmuir monolayer (Q_o) maximum adsorption capacity parameter (Table 4). Finally, the dimensionless Langmuir separation constant (R_L) indicated that the adsorption process is favourable for WHB [21].

3.3 Adsorption Thermodynamic Studies

The effect of temperature changes on the adsorption was studied in the range 298-338 K to determine the relative thermodynamic feasibility of CIP and CAF adsorption process onto WHB. As the temperature was varied from 298 to 338 K, the removal efficiency

decreased (Table 5) an indication of an exothermic process.

This decrease in retention efficiency is due to the weakening of the binding forces between the WHB and the PhC molecules and the equilibrium shifting towards desorption. The thermodynamic parameter ΔG was estimated using Eq. (5) while the ΔH and ΔS were obtained from the slope and intercept, respectively, of the Van't Hoff plot (Fig. 5).

Negative and positive ΔG changes indicate spontaneous and non-spontaneous processes, respectively. From Table 5, it is evident that both CIP and CAF adsorption onto WHB are spontaneous. The negative ΔH values confirm that the reaction is exothermic. Since ΔH values rangingfrom 40-120 kJ mol^{-1} is reported to describe chemisorption mechanism, [22] the magnitude of ΔH values in the present work (Table 5) confirms a physisorption mechanism. The negative ΔS value implies increased orderliness at the adsorbent/adsorbate interfaces. The adsorption processes are evidently energetically stable.

$y = 3218.x - 9.033$
$R^2 = 0.979$
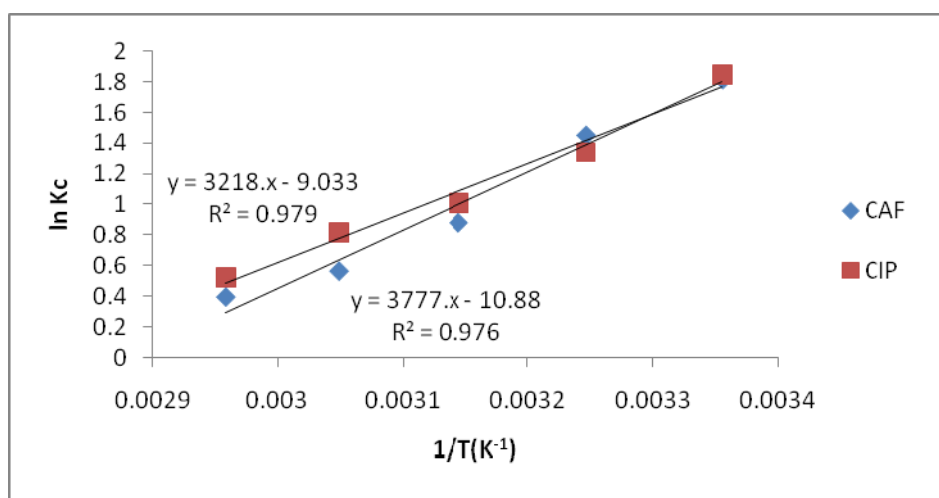
$y = 3777.x - 10.88$
$R^2 = 0.976$

Fig. 5   The Van't Hoff plot for the adsorption of CAF and CIP onto WHB.
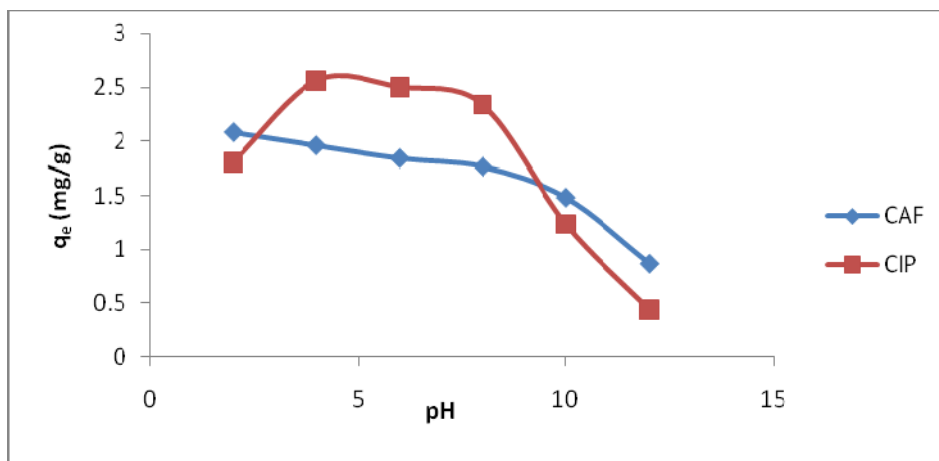

Fig. 6   Variation of amount of CAF and CIP adsorbed onto WHB as a function of pH.

3.4 Adsorption Mechanism Studies

Solution pH is known to affect the adsorption of PhCs onto the carbonaceous material. The effect of pH was conducted in the range 2.0 to 12.0. The adsorption capacity was strongly pH dependent with maximum adsorption at pH 4 and pH 2 for CIP and CAF, respectively (Fig. 6).

To explain the trend, the point of zero charge (pH$_{pzc}$) was used. This is an indicator of the surface charge of the adsorbent at aspecific pH. The mechanism of adsorption of organic molecules from dilute aqueous solutions on carbonaceous materials is known to be a complex interplay between electrostatic, non-electrostatic and hydrophobic interactions and these interactions depend on the characteristics of the adsorbent and adsorbate [18].

The pH$_{pzc}$, was 7.0 for WHB (Fig. 7) and the surface charge was therefore positive below pH 7 and negatively charged above the pH$_{pzc}$. Though there seem to be a discrepancy in literature, the pK$_a$ value for CIP lies between 6.1 and 8.7 while that of CAF is 14 [9]. Therefore, between pH 6.1-8.7, CIP was conceived to be a neutral molecule (CIP^0) yet the adsorption capacity was highest (Fig. 6). This shows that the binding of CIP^0 onto WHB within this range is a non-electrostatic interaction. At pH below 6.1 CIP molecules were positively charged (CIP$^+$) as well as the adsorbent surface and the adsorption capacity is significantly reduced due to electrostatic repulsion. A similar trend is observed at pH above 8.7 where the
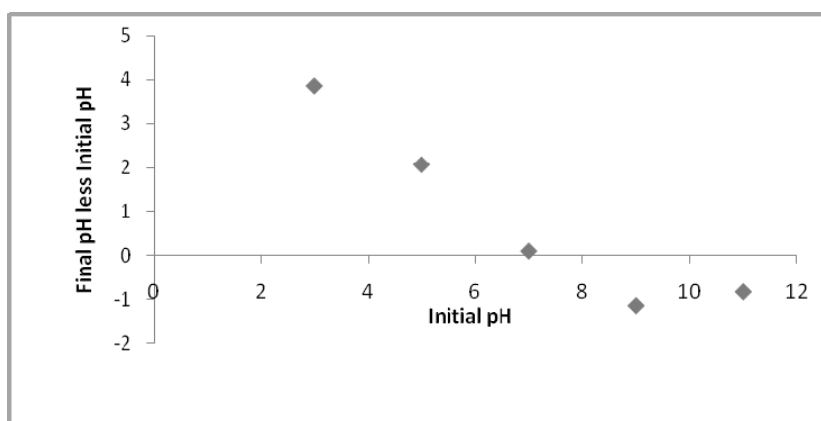
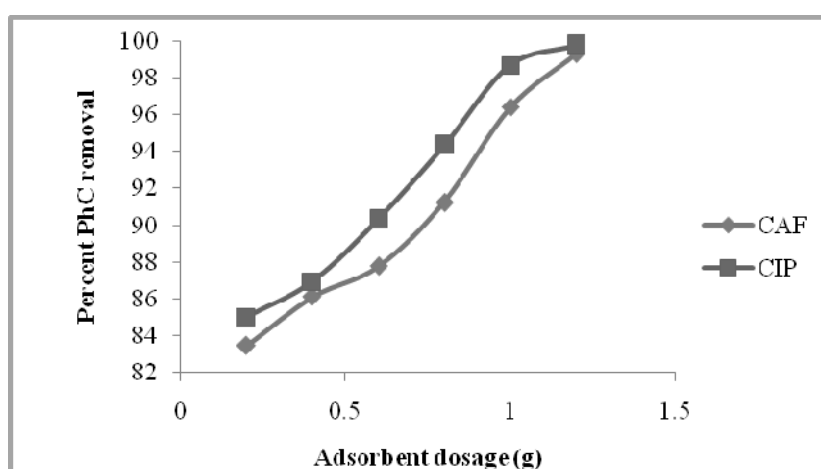Fig. 7   Plot depicting the pH_{pzc}.

Fig. 8   Variation of percent of CAF and CIP adsorbed onto WHB as function of adsorbent dosage.

negatively charged WHB surface repels the CIP anionic molecules. Therefore, beyond the pK_a range, the adsorption of CIP is controlled by electrostatic forces.

At pH lower than 14, CAF existed in cationic form (CAF^+) while the WHB surface was positively charged below pH 7 where adsorption is highest. This clearly indicates a non-electrostatic driven interaction. The observed decrease in CAF adsorption with rise in pH is a phenomenon hitherto unexplained and foretells that other adsorption mechanisms and molecular properties play dominant roles. The biochar depicted a higher affinity for CIP (log K_{ow} 0.28) than CAF (log K_{ow} -0.07). It is therefore conceivable that hydrophobic interactions also govern the adsorption of CAF and CIP onto WHB. Other studies involving carbonaceous adsorbents have reported similar observations [4].

3.5 Optimization of the Adsorbent Dosage

As the amount of WHB was increased from 0.1 to 1.2 g, the amount adsorbed increased as well from 83 % to 99% $mg \cdot g^{-1}$ for CAF and 85% to 99% $mg \cdot g^{-1}$ (Fig. 8). This is consistent with the number of increasing sites of adsorption.

4. Conclusions

This work established that WHB is an efficient carbonaceous adsorbent for removal of both CAF and CIP from aqueous solutions. The Equilibrium data was well represented by both Freundlich and Langmuir isotherm models. The adsorption kinetics was also found to fit well into the pseudo-second-order model while intraparticle

diffusion model was not the sole rate determining step. The magnitude and negative thermodynamic parameter values (ΔG, ΔH and ΔS) described a favourable, exothermic, spontaneous and a physisorption type of adsorption. pH dependence studies displayed a multi-mechanistic type of adsorption reaction. The study provides a suitable alternative use of water hyacinth (*Eichhornia crassipes*) biomass with a dual benefit of protection of Lake Victoria ecosystem and an alternative low-cost residue-based biochar for water treatment regimes.This is particularly necessary in developing countries, especially Kenya where proper waste disposal and providence of clean drinking water has not been given a top priority.

Acknowledgement

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