Simultaneous Sorption of Ciprofloxacin and Amoxicillin on Chitosan Composites from Aqueous Solutions: Kinetics and Isotherms

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***Abstract*—**The occurrence of pharmaceutical compounds, particularly antibiotics, in treated water has posed a significant toxic health risk to humans, fauna, and flora. This is ascribed to the inability of conventional wastewater treatment plants to completely eradicate these contaminants of environmental concern during treatment. Despite the effectiveness of the solid-liquid adsorption process in the removal of antibiotics and other pharmaceutical compounds (PCs), studies on simultaneous adsorption of PCs are scanty. As such, the present work is focusing on investigating the simultaneous sorption of ciprofloxacin and amoxicillin on chitosan carbon nanotubes (CCNT) composites. The model adsorbent demonstrated affinity in the order amoxicillin > ciprofloxacin for the binary sorption system. The observed high affinity in terms of amoxicillin was ascribed to the hydrophobic nature of amoxicillin (logKow = 0.87) compared to ciprofloxacin (logKow = 0.28). It is worth noting that the solution pH demonstrated to have a significant effect on the speciation distribution of the model contaminants. Moreover, the nonlinear pseudo-first-order kinetic model best fitted the data for single adsorption ($R^2 \geq 0.948$) and the Extended Langmuir isotherm model ($R^2 \geq 0.903$) was the selected model to predict the simultaneous sorption of ciprofloxacin and amoxicillin on CCNT from aqueous solution. As such, CCNT demonstrated to be an effective adsorbent for the simultaneous sorption of antibiotics from aqueous solutions.

***Keywords*—**Amoxicillin, Antibiotics, Chitosan, Ciprofloxacin.

I. Introduction

Recently, there has been rapid growth in population, agro-industrialisation, as well as the surfacing of novelty viruses, such as the coronavirus (COVID-19), which has contributed to the rise in the occurrence of emerging contaminants (ECs) in water receiving bodies ranging from organic to inorganic contaminants [1]. The occurrence of ECs in water bodies is ascribed to their continuous discharge into the ecosystem from a range of point sources such as households, hospitals, chemical and agricultural industries, pharmaceutical and personal care producing industries and other industries [1]. Pharmaceutical compounds (PCs), such as antibiotics, hormones, anticonvulsants, nonsteroidal anti-inflammatory drugs, lipid-regulators, and β-blocker have received significant attention from many researchers due to their occurrence in aquatic environments posing undesirable effects in the ecosystem [1]. PCs are characterised with peculiar physico-chemical properties such as long half-life, hydrophilic nature, high polarity, persistence and low volatility which makes their complete remediation by wastewater treatment plants (WWTPs) to be difficult compared to conventional contaminants i.e., solids, biological nutrients, chemical oxygen demand (COD), as well as biological oxygen demand (BOD) [2]. According to Yin, et al. [3], the incomplete remediation of PCs by conventional WWTPs is ascribed to their transformation into metabolites which have been detected in WWTP effluent streams and in drinking water [4]. As such, there is a need to develop eco-friendly treatment technologies post conventional WWTPs aimed at the eradication of PCs and their metabolites from aqueous environments.

Studies have been conducted on the application of advanced treatment technologies for PCs remediation from aqueous environments. Some of the reported technologies in literature include catalytic ozonation [5], photocatalytic reaction [6], solid-liquid adsorption by activated carbon [7], reverse osmosis [8], pressure driven membrane [9], and biological reactors [10]. Despite the effectiveness of the investigated technologies in PCs removal from aqueous solutions, these processes are associated with a few drawbacks limiting their application on an industrial scale. Catalytic ozonation is characterised with short life span of ozone which renders this technology expensive, and its high energy demand is the major drawback to upscale [11]. Photocatalytic processes require the separation of the photocatalyst from the slurry after each batch as well as photocatalyst regeneration subsequently escalating operational costs [12]. Reverse osmosis and pressure driven membrane processes have been successfully used for water purification at a tertiary stage, however, low permeation flux, inadequate selectivity and membrane durability, membrane fouling, and high equipment and operating cost have rendered the upscaling of these

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processes uneconomic [13]. From the reviewed literature by Khumalo, et al. [4] it is apparent that PCs can be removed by biological processes from aqueous environments, however, biological processes are associated with sludge generation subsequently increasing operational costs as well as high hydraulic retention time compared to other wastewater treatment process such as solid-liquid adsorption. Solid-liquid adsorption using activated carbon has demonstrated to be a successful technology for PC remediation from wastewater streams, however, the high cost of activated carbon has rendered this technology expensive to upscale [14].

On the other hand, chitosan composites have been successfully applied as adsorbents in the removal of PCs, particularly antibiotics, from wastewater streams, thus drawing the attention of many researchers [15]. The appetite on chitosan-based composites is ascribed to chitosan being a derivative of chitin which is the second most abundant polysaccharide after cellulose found in exoskeletons of crustaceans and insects, as well as fungi cell walls [16]. The distinctive properties of chitosan such as low processing costs, being non-toxicity, hydrophobicity, biodegradability, and biocompatibility has cemented its application for the most efficient adsorption of PCs [17]. Moreover, chitosan consists of highly active acetamido, amino and hydroxyl groups which are excellent chelating sites for targeted pollutants in aqueous solutions and allows for surface modification [18]. Despite the effective adsorption of PCs by chitosan composites, scientific research on multiple PCs adsorption (i.e., systems with more than one PC in aqueous solution) are scanty. Therefore, the originality of the current study is the investigation of single and simultaneous sorption of two commonly detected antibiotics i.e., amoxicillin (AMX), and ciprofloxacin (CIP) on chitosan carbon nanotubes (CCNTs) composite (hydrogel beads). Moreover, the study provides the understanding of the antagonistic and synergistic effects, and interaction mechanisms between the model contaminants and adsorbent through the application of nonlinear kinetics and isotherm empirical models to avoid the errors associated with the application of linear empirical models for effective process design.

II. Materials and Methods

A. Materials

All chemicals used were of analytical grade and no further purification was done. Ciprofloxacin, amoxicillin, and multi-wall carbon nanotubes were supplied by Lasec laboratories, Durban, South Africa. Chitosan powder from shrimp shells with a degree of deacetylation of ≥85%, sodium hydroxide (NaOH) pellets, methanol (CH_3OH), sulfuric acid (H_2SO_4) were supplied by Sigma-Aldrich, South Africa.

B. Adsorbent preparation

The CCNT composite was prepared by dissolving 100 g of chitosan in 400 mL of 1 % v/v of glacial acetic acid solution. Thereafter, the chitosan-glacial acetic acid mixture was vortexed using a magnetic stirrer at 200 rpm for 24 hours at room temperature, this was done to achieve complete dissolution of chitosan. During vortexing, the mixture of chitosan-glacial acetic acid was covered with aluminium foil to minimise any evaporation since glacial acetic acid is relatively volatile. Thereafter, 5 wt.% (with respect to chitosan) of acid functionalised multiwall CNTs were added into the chitosan-glacial acetic acid mixture, which was following by vortexing the acid mixture at 200 rpm for 2 hours. This was done to ascertain homogeneous distribution of CNTs in the mixture. The viscous CCNT mixture was allowed to degas at room temperature until all air bubbles disappeared. CCNT microbeads were synthesised by adding the viscous CCNT gel dropwise in a solution of 15 wt.% NaOH and 95 % (v/v) of methanol at volume ratio of 4 (NaOH):1(CH_3OH) using a 10-mL syringe which precipitated into CCNT hydrogel beads. The CCNT beads were soaked in the NaOH-methanol solution for 24 hours, then rinsed with deionised water until a pH of 7 was obtained prior being dried at 55℃ for 12 hours.

Batch adsorption studies

The adsorption profile of CIP and AMX by CCNT hydrogel beads was investigated by adopting the batch adsorption standard method as presented by Zhou, et al. [30]. Experiments were conducted using 250 mL blue-capped sample bottles with a sample volume size of 100 mL for a predetermined initial concentration of 40 mg/L of CIP and AMX. It is imperative to note that experiments were conducted at a predetermined solution pH of 6 and 7 for CIP and AMX, respectively. A predetermined quantity of CCNT hydrogels at a dosage of 1.5 g/L was added into respective CIP and AMX aqueous solutions and placed in a Stuart orbital shaker SSL1 from Lasec laboratories, Durban, South Africa and agitated for 12 hours at a rate of 150 rpm at room temperature. At a set time interval, samples were drawn and filtered using a 0.45 µm syringe filter and transferred into a 10 mL sample tube. The filtered sample was the centrifuged at 5000 rpm for 10 minutes, thereafter, a supernatant solution of the centrifuged sample was analysed for the residual CIP and AMX concentration using a Uv-vis spectrophotometer at a wavelength of 272 nm. Equations (1) to (11) in the subsequent subsections were used for kinetics studies. For adsorption isotherm studies, the aforementioned procedure was adopted for an initial concentration ranged of 5 mg/L to 50 mg/L of CIP and AMX, respectively at a contact time of 24 hours.

C. Adsorption mathematical models

The evaluation of the sorption of targeted pollutant onto the model adsorbent is crucial for the effective design as well as performance evaluation of a process. As such, for the present study, nonlinear kinetics and isotherm models were used to correlate the solid-liquid phase adsorption experimental data as recommended by Mudhoo and Pittman Jr [31] and Lima, et al. [32].

D.Adsorption kinetics

In a typical adsorption process, it is necessary to investigate the adsorption kinetics as well as the effect of the amount of adsorbent on the adsorption rate [33]. As such, the adsorption rate constants were ascertained by applying the pseudo-first-order (PFO) (1) and pseudo-second-order (PSO) (2) nonlinear kinetic models.

$$q_{t,i} = q_{e_{1,i}}\left[1 - exp\left(-k_{1,i}t\right)\right] \quad (1)$$

$$q_{t,i} = \frac{q_{e_{2,i}}^2 k_{2,i} t}{\left[k_{2,i} q_{e_{2,i}} t + 1\right]} \quad (2)$$

$$q_{t,i} = \frac{(C_0 - C_t)}{m} V \quad (3)$$

where $q_{t,i}$ is the adsorption capacity of compound i in mg.g^{-1} at time t; $k_{1,i}$ and $q_{e_{1,i}}$ is the PFO rate constant in min^{-1} and adsorption capacity at equilibrium in mg.g^{-1} of compound i; $k_{2,i}$ and $q_{e_{2,i}}$ is the PSO rate constant in g.mg^{-1}.min^{-1}, and the adsorption capacity at equilibrium in mg.g^{-1} of compound i. C_0 and C_t is the initial concentration and concentration at time t of compound i measured in mg.L^{-1}; m and V is the mass of the adsorbent in g, and volume of the solution in L.

E. Adsorption isotherms

Isotherms studies were conducted to study the adsorption equilibrium by employing nonlinear isotherm models which relates the amount of adsorbate retained on the surface of the model adsorbent (q_e) with the residual concentration of the targeted pollutant in liquid phase (C_e) under constant temperature conditions [34]. The Langmuir (4), Freundlich (5), Redlich-Peterson (6), and Langmuir-Freundlich (7), are amongst the commonly used isotherm models reported in literature [20].

$$q_{e,i} = \frac{q_{mL,i} K_{L,i} C_{e,i}}{1 + K_{L,i} C_{e,i}} \quad (4)$$

$$q_{e,i} = K_{F,i} C_{e,i}^{n_{Fi}} \quad (5)$$

$$q_{e,i} = \frac{K_{RP,i} C_{e,i}}{1 + a_{RP,i} C_{e,i}^{\beta i}} \quad (6)$$

$$q_{e,i} = \frac{q_{LF,i}\left(K_{LF,i} C_e\right)^{n_{LF,i}}}{1 + \left(K_{LF,i} C_e\right)^{n_{LF}i}} \quad (7)$$

$$q_{e,i} = \frac{(C_0 - C_{e,i})}{m} V \quad (8)$$

Where $q_{e,i}$ and $C_{e,i}$ is the adsorption capacity and concentration for compound i at equilibrium measured in mg.g^{-1} and mg.L^{-1}, respectively; $q_{mL,i}$ and K_{Li} are the Langmuir constants for compound i measured in mg.g^{-1} and L.mg^{-1}, respectively; K_{Fi} is the Freundlich constant for component i measured in (mg.g^{-1})(L.mg^{-1})$^{-n_F}$; $n_{F,i}$ is the dimensionless Freundlich constant for compound i; K_{RPi} and a_{RPi} are the Redlich-Peterson constants for component i measured in L.g^{-1} and (L.mg^{-1})$^{\beta}$; β_i is the dimensionless Redlich-Peterson constant for component i; $q_{LF,i}$, $K_{LF,i}$, and $n_{LF,i}$ is the Langmuir-Freundlich maximum adsorption capacity of adsorbent (mg.g^{-1}), Langmuir-Freundlich constant (L.mg^{-1}), and the dimensionless Langmuir-Freundlich constant, respectively.

Binary adsorption isotherms were studied by applying the Extended Langmuir (9) and Extended Sips (10) isotherm models to determine the biosorption capacity of the CIP-AMX system on CCNT. The biosorption isotherm models were developed from the conventional mono-sorption models in order to account for the multi-sorption systems as recorded by Martín-Lara, et al. [35] and Pauletto, et al. [14].

$$q_{e,i} = \frac{q_{max} K_{EL,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{EL,j} C_{e,j}} \quad (9)$$

$$q_{e,i} = \frac{q_{m,i} K_{ES,i} C_{e,i}^{\frac{1}{n_i}}}{1 + \sum_{j=1}^{N} K_{ES,j} C_{e,j}^{\frac{1}{n_j}}} \quad (10)$$

Where q_{max} is the theoretical maximum biosorption capacity measured in mg.g^{-1} , $K_{EL,i}$ (L.mg^{-1}) and $K_{EL,j}$ (L.mg^{-1}) are the Extended-Langmuir constants of component i and j, respectively; $C_{e,j}$ (mg.L^{-1}) is the equilibrium concentration of component j; $q_{m,i}$ (mg.g^{-1}) is the theoretical maximum biosorption capacity of component i; $K_{ES,i}$ (L.mg^{-1})$^{1/n}$ and $K_{ES,j}$ (L.mg^{-1})$^{1/n}$ are the Sips constants of component i and j, respectively; n_i and n_j are the Sips constants for component i and j, respectively obtained by fitting of experimental data for biosorption system.

III. RESULTS AND DISCUSSION

A. Adsorption kinetics

The underlying kinetics for the single sorption of CIP and AMX on CCNT hydrogel beads were examined by employing the nonlinear PFO (1) and PSO (2) adsorption kinetics empirical models. From the results presented in Table I, the PFO kinetic model gave an adsorption capacity of 23.739

mg.g^{-1} for CIP and 23.064 mg.g^{-1} for AMX at equilibrium, which is relatively close to the experimental values of 22 mg.g^{-1} for CIP and 20 mg.g^{-1} for AMX. Moreover, it is worth noting that, from the kinetic models' parameters presented in Table I, the PFO gave R^2 values of 0.994 and 0.983 for CIP and AMX, respectively. The PFO R^2 values obtained were higher than those of PSO for both CIP and AMX suggesting that the experimental data for both model antibiotics were best fitted by the PFO. Furthermore, the PFO and PSO kinetic models were validated by applying the difference of the BIC value of PFO and BIC value of PSO. As such, the ΔBIC of 2.44 for the CIP system suggests that the PFO is the most suitable model as compared to the PSO kinetic model. On the other hand, the AMX system gave a ΔBIC value of 8.86 suggesting that the PFO best fitted the experimental data. According to Bauldry [25], the BIC can be used in assessing two competing models by following the guidelines outlined by Raftery [26], suggesting that ΔBIC values between two models of 0 – 2 constitutes weak evidence in favour of the model with the smaller BIC; a BIC difference between 2 and 6 constitutes positive evidence; and BIC difference between 6 and 10 constitutes strong evidence. Hence, based on the reported ΔBIC values (Table I) for the sorption of CIP and AMX, it is evident that both systems favoured the PFO kinetic model. The findings of the current study suggest that the sorption of CIP and AMX on chitosan carbon nanotubes hydrogels is a diffusion-controlled process [27].

TABLE I
CIP AND AMX ADSORPTION KINETICS PARAMETERS

Species	Model	Parameter				
		k (min^{-1})	q_e (mg/g)	R^2	*BIC*	ΔBIC
CIP	PFO	0.003851	23.739	0.994	-26.5	2.44
	PSO	0.000102	32.246	0.993	-24.08	
AMX	PFO	0.003188	23.064	0.983	-3.28	8.86
	PSO	7.1×10^{-5}	33.456	0.977	5.57	

Furthermore, the experimental data was fitted in the Weber and Morris kinetic model (11) to identify the diffusion mechanism in the adsorption process as proposed by Weber Jr and Morris [28].

$$q_t = k_i t^{0.5} + C_i \quad (11)$$

Where k_i (mg.g^{-1}.min$^{-1/2}$) and C_i (mg.g^{-1}) are intraparticle diffusion rate constants. According to Sahoo and Prelot [29] and Weber Jr and Morris [28], intraparticle diffusion is involved during the adsorption process if the plot of q_t as a function of $t^{0.5}$ yields a straight line. However, experimental data for the sorption of CIP and AMX gave a nonlinear relationship but multilinear plots for both model antibiotics as depicted in Fig.1. As such, the results presented in Fig.1 suggest that multiple processes are limiting the overall adsorption rate. Traversing Fig.1 from left to right, the very first segment of the plot with the highest slope depicts a zone that is controlled by external mass transfer. In the external mass transfer zone (Fig.1) the constant C_i of the fitted model is approximately zero indicating insignificant effects of the boundary layer diffusion on the adsorption of both CIP and AMX but both antibiotics were adsorbed on the surface of the adsorbent. The subsequent segment represents a zone controlled by intraparticle mass transfer, suggesting that CIP and AMX gradually diffused into the model adsorbent, and the last segment which is almost plateau denotes an incipient of an equilibrium state indicating that the model antibiotics were adsorbed in the active sites of the model adsorbent.

However, it is noted that the adsorption mechanism for any adsorption process cannot be explicitly explained by the PFO and PSO empirical models. However, available literature [30-32] suggest that adsorption mechanisms are solely established by using analytical techniques e.g., FTIR, SEM, XRD, pH_{PZC} etc., and having a clear chemical nature of the adsorbate and adsorbent, adsorbent's surface, and chemical or physical interactions between the adsorbent and adsorbate. Lima, et al. [31] and Tran, et al. [33] also reported that the use of analytical techniques together with adsorptive thermodynamic data, activation and adsorption energies is necessary to confirm physical or chemical adsorption.

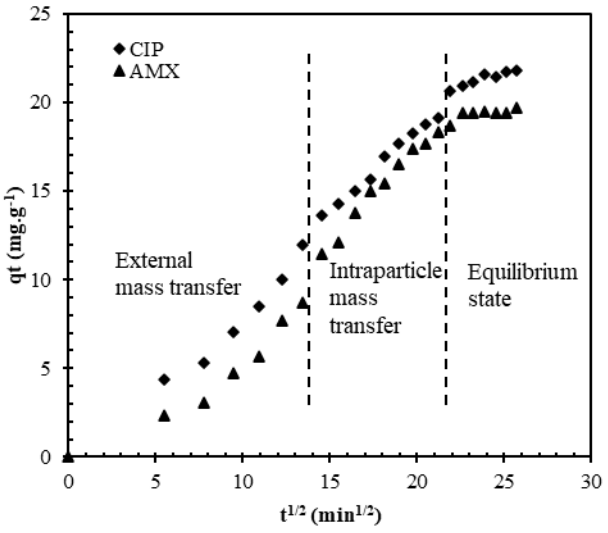

Fig. 1 Weber and Morris kinetic model curves for CIP and AMX

B. Single and binary adsorption isotherms

Selected adsorption isotherm models i.e., two-parameter adsorption isotherms (Langmuir and Freundlich models) as well as three-parameter adsorption isotherms (Redlich-Peterson, and Langmuir-Freundlich models) were applied in

modelling adsorption experimental data at equilibrium. Nonlinear adsorption isotherm models were employed to minimise errors associated with the conventional linear approach as discussed by Tran, et al. [34] and Mudhoo and Pittman Jr [20]. Single adsorption isotherm parameters are presented in Table II for the selected models. Based on the isotherm parameters presented in Table II, coefficients of determination of greater than 0.97 were recorded for all selected isotherm models. As such, the findings of the current study suggest that single adsorption experimental data was well fitted for the selected isotherm models for both CIP and AMX.

Moreover, the investigated three-parameter isotherm models best fitted the experimental data, recording relatively high coefficient of determination values (Table II) when compared to the two-parameter isotherm models. The findings of the current study are congruent with the work reported by Tran, et al. [33] for the sorption of methylene green on commercial activated carbon. On the other hand, Pauletto, et al. [7] did not report any differences in terms of the coefficients of determination in the Langmuir and Redlich-Peterson isotherm models but the Freundlich model for the solid-liquid adsorption of nimesulide and paracetamol. Under operating conditions of 298 K, for the adsorption of nimesulide, Pauletto, et al. [7] recorded R^2 values of 0.991 for both the Langmuir and Redlich-Peterson models. On the other hand, an R^2 value of 0.946 was reported for the Freundlich model. As such, for the work reported by Pauletto, et al. [7] the Redlich-Peterson three-parameters isotherm model did not demonstrate any supremacy over the Langmuir two-parameter isotherm model.

Analysis of the estimated parameters (Table II) for the selected nonlinear adsorption isotherm models, particularly the maximum adsorption capacities, the nonlinear Langmuir adsorption isotherm model indicated coherence with the experimental data recording adsorption maximum capacities 28.885 $mg.g^{-1}$ and 40.631 $mg.g^{-1}$ for CIP and AMX, respectively. As such, the model parameters of the current study suggest that the nonlinear Langmuir model can explain the adsorption of CIP and AMX on CCNT with some higher degree of certainty compared to the other investigated isotherm models. Therefore, the findings may be instructive that the adsorption of the model antibiotics occurred at the homogeneous active sites on the adsorbent surface [35]. The Langmuir equilibrium parameter is within the range of 0 and 1 i.e., 0.49 for CIP and 0.0928 for AMX thus suggesting high affinity of the model adsorbent's surface on CIP and AMX. On the other hand, the Freundlich model recorded a low heterogeneity factor, n_F of less than 1 suggesting the homogeneity of the CCNT surface. Pauletto, et al. [7] reported that lower values of n_F signifies a stronger surface heterogeneity.

TABLE II
PARAMETERS OF SELECTED SINGLE ADSORPTION ISOTHERM MODELS OF CIP AND AMX ON CCNT

		Antibiotic	
Isotherm Model	Model Parameters	CIP	AMX
Langmuir	q_{mL}	28.885	40.631
	K_L	0.495	0.0928
	R^2	0.983	0.981
Freundlich	K_F	10.090	4.657
	n_F	0.395	0.615
	R^2	0.971	0.992
Redlich-Peterson	K_{RP}	20.086	278
	a_{RP}	1.029	58.794
	β	0.846	0.388
	R^2	0.987	0.993
Langmuir-Freundlich	q_{mLF}	34.949	318.11
	K_{LF}	0.296	0.00141
	n_{LF}	0.769	0.644
	R^2	0.987	0.992

Fig. 2 and Table III depict the equilibrium data of the current study on the simultaneous sorption of CIP and AMX from a binary aqueous solution. The results presented in Fig.2 explicitly indicate that CCNT demonstrated high affinity on AMX in the binary system as compared to the single adsorption system. This is evident from the recorded AMX equilibrium maximum adsorption capacity of 28.1 $mg.g^{-1}$ for a binary adsorption system and 24 $mg.g^{-1}$ for the single adsorption system. On the other hand, a slight decrease on CIP equilibrium maximum adsorption capacity from 25.6 $mg.g^{-1}$ (single adsorption system) to 21 $mg.g^{-1}$ (binary adsorption system) was observed. As such, the findings suggest that, AMX adsorption was enhanced by the presence of CIP in the binary solution thus demonstrating synergistic adsorption effects as indicated by Pauletto, et al. [7] in the biosorption of paracetamol and nimesulide from solution. It is worth noting that slight decrease in CIP sorption in the binary system indicates that the sorption on CIP was suppressed by the presence of AMX, thus suggesting antagonistic adsorption. The findings of the current study are congruent to the work reported by Chandrasekaran, et al. [36] on the removal of CIP and AMX using acid-activated carbon from *Prosopis juliflora*.

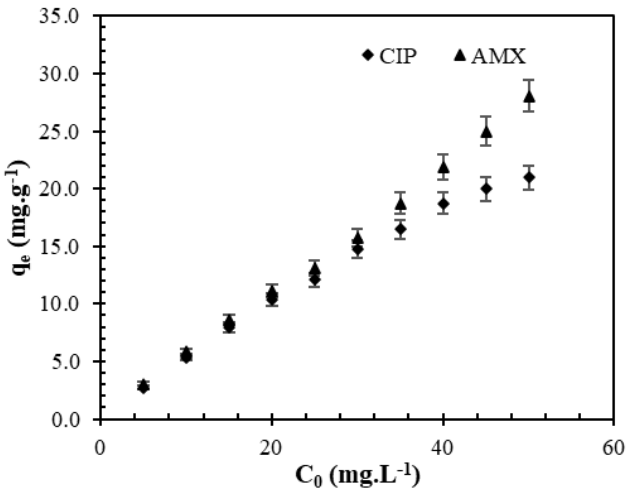

Fig. 2 Removal of CIP and AMX from a binary solution

Moreover, the binary adsorption experimental data was fitted using the competitive Extended-Langmuir and Extended Sips isotherm models. Table III depicts the competitive isotherm model parameters. From the competitive isotherm model predicted maximum adsorption capacities, it can be seen from Table III that AMX was better adsorbed as compared to CIP. According to Martín-Lara, et al. [24] in a typical biosorption system, there are three possible behaviours which can be given by the values of the ratio of the biosorption capacity of one species, q_m in the presence of the other species and the biosorption capacity for the same species when present alone in the solution, q_s; 1) if the value of q_m/q_s is greater than 1, the biosorption is promoted by the presence of the other species; 2) if the value of q_m/q_s is equal to 1, there is no observable net interaction; lastly 3) if the value of q_m/q_s is less than 1, the biosorption is suppressed by the presence of the other species. As such, the Extended-Sips model recorded q_m/q_s ratios of 0.634 for CIP and 158 for AMX suggesting the biosorption of AMX was promoted by the presence of CIP in solution which is congruent to the experimental data presented in Fig.2 for an initial concentration $\geq$ 20 mg/L. Moreover, the CIP q_m/q_s ratio of 0.634 suggests that the presence of AMX in solution has an antagonistic effect on the biosorption of CIP while AMX q_m/q_s ratio of 158 explicitly demonstrates the synergistic effect of CIP in the sorption of AMX on CCNT.

On the other hand, the competitive Extended-Langmuir isotherm model recorded q_m/q_s ratios greater than 1 for both model antibiotics suggesting that the biosorption of both antibiotics was promoted by the presence of the other species which is not congruent to experimental data for an initial concentration greater than 20 mg/L, Fig.2. However, the Extend-Langmuir isotherm model recorded theoretical equilibrium adsorption capacities with less deviation from experimental data when compared with the Extended-Sips isotherm model suggesting a better fit of the experimental data. The supremacy of the Extended-Langmuir is evident from the recorded R^2 values of $\geq$ 0.903 (Table III) for both model antibiotics, which demonstrates a good fit for experimental data.

TABLE III
MODEL PARAMETERS FOR COMPETITIVE EXTENDED-LANGMUIR AND EXTENDED-SIPS ISOTHERM MODELS

		Antibiotic	
Isotherm Model	**Model Parameters**	**CIP**	**AMX**
Extended-Langmuir	q_{max}	30.869	2245
	K_{EL}	0.111	0.00137
	R^2	0.987	0.903
	q_m/q_s	1.069	55.253
Extended-Sips model	q_{max}	22.153	44320
	K_{ES}	0.376	0.663
	n_i	0.362	1.0625
	R^2	0.996	0.904
	q_m/q_s	0.634	158

IV. CONCLUSION

Single and binary adsorption of CIP and AMX from aqueous solutions on CCNT hydrogel beads was investigated. Single adsorption studies demonstrated higher affinity of CCNT on CIP adsorption, the Langmuir nonlinear adsorption isotherm model best fitted the experimental data recording theoretical equilibrium capacities with minimal deviation from experimentally obtained equilibrium adsorption capacities. Moreover, the nonlinear PFO kinetics model best fitted the single adsorption experimental data suggesting that the adsorption of CIP and AMX on CCNT is a diffusion-controlled process which was confirmed by the Weber and Morries kinetic model with multiple linear curves of the experimental data. For binary adsorption studies, the competitive Extended-Langmuir and Extended-Sips isotherm models were applied and best fitted the experimental data. Despite the Extended-Sips isotherm model recording relatively high R^2 values and suggesting the suppression of CIP sorption in the presence of AMX, the model recorded relatively high theoretical equilibrium adsorption capacities with relatively high deviations from experimental data. On the other hand, the competitive Extended-Langmuir isotherm model also recorded high R^2 values with a slight deviation between experimental data and the theoretical equilibrium adsorption thus demonstrating a good fit for the experimental data as compared to the Extended-Sips isotherm model. The observed affinity of CCNT AMX in the binary system, can be ascribed to the high hydrophobic nature of AMX as compared to CIP.

Despite the CCNT hydrogel beads demonstrating high affinity of CIP and AMX both on single and binary adsorption systems, the is still a need to conduct further investigation on the effect of competing ions on the sorption of the model

antibiotics in aqueous solutions as studies on this topic are scanty. Moreover, more work still has to be done focusing on the sorption mechanism of antibiotics on the model adsorbent on the basis that, kinetic models alone cannot explicitly suggest the sorption mechanism of model pollutants in a typical solid-liquid adsorption process.

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