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Competitive sorption affinity of sulfonamides and chloramphenicol antibiotics toward functionalized biochar for water and wastewater treatment

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Abstract

Competitive sorption of sulfamethazine (SMT), sulfamethoxazole (SMX), sulfathiazole (STZ) and chloramphenicol (CP) toward functionalized biochar (fBC) was highly pH dependent with maximum sorption at pH ~4.0-4.25. Equilibrium data were well represented by the Langmuir and Freundlich models in the order STZ > SMX > CP > SMT. Kinetics data were slightly better fitted by the pseudo second-order model than pseudo first-order and intra-particle-diffusion models. Maximum sorptive interactions occurred at pH 4.0-4.25 through H-bonds formations for neutral sulfonamides species and through negative charge assisted H-bond (CAHB) formation for CP, in addition to π-π electron-donor-acceptor (EDA) interactions. EDA was the main mechanism for the sorption of positive sulfonamides species and CP at pH < 2.0. Sorption of negative sulfonamides species and CP at pH > 7.0 was regulated by H-bond formation and proton exchange with water by forming CAHB, respectively. The results suggested fBC to be highly efficient in removing antibiotics mixture.

Keywords: Sorption; Sulphonamides; fBC; Electron-donor-acceptor; CAHB

1. Introduction

The use of different antibiotics resulted in reduction of the mortality and morbidity rates from epidemic and infectious diseases such as syphilis, tuberculosis, pneumonia, gonorrhea, and communicable diseases of childhood (Carvalho and Santos, 2016; Cui et al., 2016; Rajapaksha et al., 2014). The occurrence of antibiotic residues in the environment is attracting attention due to their potential long-term adverse effects on human and animals (Ahmed et al., 2015; Ahmed et al., 2017a; Zhao et al., 2016; Wang et al., 2017). In addition, antibiotics are of great concern as they are consumed in significant quantities all over the world and can particularly act on microorganisms without affecting cells and tissues (Ahmed et al., 2017a; Seifrtová et al., 2009). Physical treatment processes have been found very effective and economic in removing antibiotics among which sorption has emerged as a cost effective method for pollutant removal; unaffected by the potential toxicity as for biological processes; and easy to design and operate (Ahmed et al., 2017a; Yu et al., 2016; Xie et al., 2016). In addition, sorption is an extremely important process because it may dramatically affect the fate and impacts of contaminants in the environment through different mechanisms (Maskaouri and Zhou, 2010). The efficiency of sorption process is highly affected by the properties of sorbate, sorbent, and operating conditions (Azhar et al., 2016). The degree of sorption mainly depends on the physicochemical properties of the micropollutants, type of solid matrices, surface area, porosity, pore diameter, and environmental conditions (Pavlović et al., 2014; Veksha et al., 2014; Yu et al., 2016).

The sorption of antibiotics onto carbonaceous materials such as biochar (Yu et al., 2016; Ahmed et al., 2016a; Ahmed et al., 2017b; Yao et al., 2012), activated carbon (Grover et al., 2011), carbon nanotubes (Ahmed et al., 2015), graphene, clay minerals (Ahmed et al., 2015), and hollow polymer nanorods (Xie et al., 2016) has been widely studied and proved very effective (Ahmed et al., 2015). The sorption of antibiotics using biochar was found particularly efficient

(Ahmed et al., 2015; Ahmed et al., 2016b). Biochar has a high hydrophobicity and aromaticity and is an excellent sorbent for hydrophobic organic contaminants e.g. aromatics (Lian et al., 2014; Wang et al., 2016). To date, the majority of adsorption studies on the removal of different antibiotic residues by carbonaceous sorbents have been conducted using single solutes, and only a few studies were reported based on the competitive nature of micropollutants (Ahmed et al., 2017b; Calisto et al., 2017; Nielsen and Bandosz, 2016). In addition, the removal mechanisms of antibiotic mixture using different adsorbents are unclear. In reality, aquatic environment can be highly complex including mixtures of different organic and inorganic contaminants, and thus understanding the mechanisms of competitive adsorption is of great importance. During the application of sorbent, sorbate molecules can interact with the same sites of the sorbent particles, hence faster sorption mainly occurs for the compounds which have specific affinity to be sorbed onto the specific surface of sorbent. Interactions are very simple for single solute but can be very complex for a mixture of contaminants. Therefore, we have targeted four antibiotics for their sorption onto functionalized biochar (fBC) in order to check their competitive sorption affinity and to assess the sorption mechanisms as well as sorption trend in different water types.

This study aims to bridge the knowledge gap by studying the competitive sorptive capacity and mechanisms by fBC for four widely used antibiotics SMT, SMX, STZ and CP from water and wastewater. Specifically we studied: (i) the effect of pH on competitive sorption with detailed sorption affinity mechanisms, (ii) the kinetics parameters for competitive solutes, (iii) the competitive sorption isotherms parameters, and (iv) the application of fBC in removing antibiotics mixtures from lake water and synthetic wastewater under practical conditions.

2. Materials and methods

2.1. Chemicals and reagents

The antibiotic standards of SMT, SMX STZ and CP were purchased from Sigma-Aldrich, Australia. HPLC-grade organic solvents such as acetonitrile and formic acid were also purchased from Sigma-Aldrich, Australia. Ortho phosphoric acid (85%), hydrochloric acid (35%), sodium hydroxide, potassium chloride, sodium chloride were obtained from Sigma-Aldrich. *Eucalyptus globulus* wood was donated by New Forest Asset Management Pty Ltd, Portland, Victoria, Australia.

2.2 Preparation and characterization of fBC

fBC was prepared according to Ahmed et al. (2017b). Briefly, 25 g of eucalyptus wood biomass was pyrolyzed at 400 ^{o}C at an average heating rate of ~11.0 °C min^{-1} under constant nitrogen pressure of 2 psi for 2 h, to obtain biochar samples. Biochar functionalization was carried out by soaking 10 g of biochar in 20 mL of 50% ortho-phosphoric acid ($o$$H_3PO_4$) for 3 h at 50 °C. The mixture was then reheated at 600 °C for 2 h. After that, the prepared material was left to cool inside the reactor, washed and the pH adjusted to ~7.0, followed by drying overnight at 105 °C, to obtain fBC. The physicochemical characteristics of fBC were extensively examined using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, energy dispersive spectrometry (EDS), and zeta potential instrument. The elemental composition of fBC was measured using EDS (Zeiss Evo-SEM). The identification of surface functional groups was conducted using FTIR (Miracle-10, Shimadzu), by measuring the absorbance from 400 to 4000 cm^{-1} using a combined 40 scans. Raman shifts measurement was carried out using Renishaw inVia Raman spectrometer (Gloucestershire, UK) equipped with a 17 mW Renishaw Helium-Neon Laser 633 nm and CCD array detector. Zeta potential values were measured using 500 mg L^{-1} of fBC dosage at different pH values, after pre-equilibration for 48 h, on Nano-ZS Zeta-seizer

(Malvern, Model ZEN3600). Zeta potential was measured three times at each pH (50 scans each time), with the average and standard deviation being calculated.

2.3. Competitive sorption experiments using fBC

The stock solutions (100 mg L^{-1}) of SMX, SMT, STZ and CP were diluted to different initial concentrations of each antibiotic. The effects of pH were studied at adjusting pH values from 1.5 to 10.9, using HCl and NaOH solutions. fBC was pre-equilibrated at the same pH for 24 h using half of the volume of a mixture of antibiotics and rest of solute was added and shaken for another 42 h. The kinetics studies were carried at a pH 4.0-4.25 (where maximum interactions occurred based on pH study) at 25 °C over 33 h using 80 mg L^{-1} of fBC. Batch competitive experiments were conducted at 25 °C using 80 mg L^{-1} of fBC with initial concentrations of 0.250-20.0 mg L^{-1} for each antibiotic in mixture mode which were shaken on an orbital shaker at 120 rpm for 42 h (apparent equilibrium time) at pH 4.0-4.25. In all cases, a constant ionic strength was maintained using 0.01 M NaCl. The control experiments without adsorbents were also executed. The application of fBC to treat lake water (TOC, 96.67 mg L^{-1}) and synthetic wastewater (TOC, 54.0 mg L^{-1}) was carried out by spiking each antibiotic (1.0 mg L^{-1}) at pH ~4.0-4.15 and 25 °C. TOC was measured by using a TOC analyzer by the filtration of the collected and prepared sample using 1.0 mm pore size syringe filter. Synthetic wastewater was composed of peptone, beef extract, humic acid, tannic acid, arabic acid, sodium lignin sulphonate, acacia gum powder, KH_2PO_4 and $MgSO_4.3H_2O$. Control experiments in the absence fBC with different water matrices showed that there was no loss of antibiotics. At equilibrium, the solution pH was measured before the supernatant was taken and filtered through a 0.20 μm PTFE filter for antibiotic analysis using HPLC.

2.4. Antibiotics determination and data fitting

The concentrations of antibiotics were measured by HPLC (Jasco) equipped with an auto-sampler and a UV detector at 285 nm, by using 70 µL injection. A reverse phase Zorbax Bonus RP C_{18} column (5.0 µm, 2.1 ×1.50 mm, Agilent Technologies) was used for the separation. Mobile phase A was composed of acetonitrile and formic acid (99.9: 0.1) while mobile phase B was composed of Milli-Q water and formic acid (99.9: 0.1).The elution started with 15% of A and 85% of B at a flow rate of 0.4 mL min^{-1}, which was changed to 0.3 mL min^{-1} at 0.1 min and maintained till 5.9 min. Then at 6.0 min the elution changed to 40% of A and 60% of B at a flow rate of 0.3 mL min^{-1} and maintained over 15 min. The competitive sorption data for all antibiotics were fitted to the Langmuir and Freundlich isotherm models and three kinetic equations. The competitive sorption distribution coefficient (K_d, L kg^{-1}) is defined by equation 1:

$$K_d = 1000 * \frac{q_s}{C_w} = 1000 * \left(\frac{C_0 - C_w}{C_w}\right)\frac{V}{M} \quad (1)$$

where q_s is the equilibrium concentration of each antibiotic in mixture mode in sorbent (mg g^{-1}), C_w and C_o are the equilibrium and initial concentrations (mg L^{-1}) of each antibiotic in mixture mode, V is the solution volume (L), and M is the sorbent mass (g).

The kinetic equations such as the pseudo first order (PFO), pseudo second order model (PSO) and intra-particle diffusion model (IDM) can be represented as follows:

$$\text{PFO: } q_t = q_s(1 - e^{-K_1 t}) \quad (2)$$

$$\text{PSO: } q_t = \frac{K_2 q_s^2 t}{1 + K_2 q_s t} \quad (3)$$

$$\text{IDM: } q_t = K_i t^{\frac{1}{2}} + C \quad (4)$$

Parameters were estimated by nonlinear regression analysis weighted by the dependent variable. Where K_i is the apparent diffusion rate constant (mg g^{-1} $min^{-1/2}$), K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1})

157 are PFO and PSO kinetic rate constant, respectively, and *C* is a constant (mg g^{-1}) that provides
158 the thickness of the boundary layer.

159 The Langmuir and Freundlich isotherm models can be been represented as follows:

160 Freundlich model: $q_s = K_F C_w^{1/n}$ (5)

161 Langmuir model: $q_s = \frac{q_{max} K_L C_w}{1+K_L C_w}$ (6)

162 where q_{max} is the maximum adsorption capacity (mg g^{-1}), *n* is a dimensionless number related to
163 surface heterogeneity, K_F is the Freundlich affinity coefficient ($mg^{1-n} L^n g^{-1}$) and K_L is the
164 Langmuir fitting parameter (L mg^{-1}).

165

166 **3. Results and discussion**

167 *3.1. Influence of pH on antibiotic K_d during competitive interaction with fBC*

168 *The K_d* values for competitive interaction of selected antibiotics on fBC were found to be pH
169 dependence (**Fig. 1a)**. All the selected sulfonamide antibiotics are ionisable while CP is nonionic.
170 Lower K_d values were found for all positive sulfonamides species (pH 0-2.0) (Fukahori et al.,
171 2011; Pei et al., 2014; Teixidó et al., 2011) and CP at pH ~1.50 (2.0×10^4 to 4.5×10^4 L kg^{-1} for
172 SMT to STZ). The surface zeta potential value of fBC was found to be pH 2.2 (**Fig. 2**). When pH
173 was below 2.2, zeta potential value of fBC was found to be positive. Moreover, all sulfonamides
174 were positively charged at pH < 2.0 (due to matched pK_{a1} values). Thus, lower K_d values were
175 highly expected due to the repulsion nature of same species and antibiotics might also get
176 protonated at very low pH. The adsorption of antibiotics at lower pH may be dominated by the
177 interaction between the protonated aniline ring of antibiotics and the π-electron rich fBC surface
178 (Zheng et al., 2013).

179 The maximum K_d values were observed at pH ~4.0-4.25 for STZ (2.2×10^5 L kg^{-1}), SMX
180 (1.9×10^5 L kg^{-1}), SMT (1.7×10^5 L kg^{-1}) and CP (1.73×10^5 L kg^{-1}). The maximum K_d at this pH

range was found due to the adsorption of neutral species of sulfonamides at pH ~2.0-6.0 (Fukahori et al., 2011; Pei et al., 2014; Teixidó et al., 2011) and nonionizable CP. The adsorption was due to the formation of strong hydrogen bonds for sulfonamides antibiotics, and due to CAHB for CP.

Further increase in pH from 4.5 to higher pH decreased the sorption. However, another small sharp increase of K_d values for all antibiotics was observed at pH ~8.5. The observed K_d values were 5.9×10^4, 2.6×10^4, 2.7×10^4, and 1.8×10^4 L kg^{-1} respectively for STZ, SMX, SMT and CP. The main reason might be due to sorption of negative species sulfonamides at pH ~6.0-11 (Fukahori et al., 2011; Pei et al., 2014; Teixidó et al., 2011) as well as CP declined due to negative surface zeta potential value of fBC leading to electrostatic repulsion. However, the sorption affinity might be due to the formation of CAHB along with EDA interactions (Xie et al., 2014). This was due to the matching of pK_{a2} values of negative species of sulfonamides and surface hydroxyl pK_a values. After that, an increase of pH up to ~11, the sorption was decreased due to highly repulsion nature of negative surface hydroxyl groups and negative species of sulfonamides. The detailed mechanisms were discussed in **section 3.4.**

3.2. Sorption kinetics in competitive mode

Kinetic experiments were carried out for 33 h with the equilibrium being reached within ~1800 min. The kinetics of mixture of antibiotics sorption by fBC was fitted to pseudo-first-order (PFO), pseudo-second-order (PSO) and intra-particle diffusion (IPD) models. Based on the correlation coefficient (R^2) and $q_{s,cal}$ (mg g^{-1}) values, the kinetics data for all competitive solutes were slightly better fitted to the PSO chemisorption kinetic model than PFO and IDM models but their R^2 values were comparable (**Fig. 1b**). Based on the $q_{s,cal}$ values in PSO model, antibiotics followed the order of STZ (13.3 mg g^{-1}) > SMX (12.2 mg g^{-1}) > CP (12.3 mg g^{-1}) > SMT (10.9

mg g^{-1}). However, the $q_{s,cal}$ values for the PFO kinetic model followed a different order: STZ (10.73 mg g^{-1}) > CP (10.03 mg g^{-1}) > SMX (9.89 mg g^{-1}) > SMT (8.73 mg g^{-1}). IDM and PFO showed slightly lower R^2 values than the PSO model. The IPD rate constant K_i (mg g^{-1} $min^{-0.5}$) also followed the same trend as the PSO kinetic model $q_{s,cal}$ values.

3.3. Sorption isotherm models for competitive sorption

Compared with the Freundlich isotherm model, interactions of antibiotics with fBC in competitive mode were better fitted to the Langmuir model with higher R^2 values for STZ and SMX. While the Freundlich isotherm model provided a better fit for SMT and CP (**Fig. 3, Table 1**). The Langmuir sorption capacity (q_{max}) was found to be 45.2, 28.29, 21.35 and 20.71 mg g^{-1} for STZ, SMX, CP and SMT, respectively in competitive mode. The K_F values were 16.76, 9, 11.04, 9.81 and 9.65 mg^{1-n} L^n g^{-1}, respectively, for STZ, SMX, CP and SMT at 25 ^oC. These findings aligned with the results observed from pH effect and kinetics experiments. Thus, from both models, the sorption affinity can be written in the following order as STZ > SMX > CP > SMT. It is assumed that all the antibiotics in competitive mode share the same sorption sites of fBC when sorbed onto its surface. However, their sorption affinity depends on the physicochemical properties of antibiotics and fBC. The total fBC sorption capacities for all antibiotics in mixture mode were calculated by summarizing individual contributions for both Langmuir model (115.54 mg g^{-1}) and Freundlich model (47.3 mg^{1-n} L^n g^{-1}). Similar result has been reported for single and competitive sorption of three sulfonamide antibiotics (Ahmed et al., 2017b). Hence, fBC is capable of adsorbing a mixture of antibiotics onto its surface.

3.4. Mechanisms of competitive sorption on fBC

The results from the sorption isotherms, sorption kinetics and the pH effect suggested that the fBC had very strong sorption affinity for antibiotics in competitive mode, while the affinity of the antibiotics sorption onto fBC varied from compound to compound. The sorption of SMT and CP followed the Freundlich isotherm which was related to the chemisorption mechanism. While the sorption of STZ and SMX followed the Langmuir isotherm model related the homogeneous covering of the fBC surface. The kinetic results indicated the sorption of antibiotics in competitive mode agreed well with PSO, PFO and IPD model. This result indicated that the role of surface functional groups, monolayer coverage and diffusion of sorbate molecules during competitive sorption antibiotics. Thus, high competitive sorption affinities of fBC toward antibiotics were due to a combination of effects such as surface homogeneous and heterogeneous sorption sites.

All the peaks from the FTIR spectra indicated that fBC contained phenolic –OH, C=O (carboxylic and ketonic), N=C=O (isocyanate), C≡C, and C=C groups on the surface (Ahmed at al., 2016a; Davi and Saroha, 2014; Chen et al., 2016; Tang et al., 2015). FTIR spectra before and after antibiotics sorption clearly show the sorptive nature of fBC. Spectra at ~1516 cm^{-1} (aromatic C=C), at ~2090-2218 cm^{-1} (C≡C), at ~2276 cm^{-1} (N=C=O), at ~1710 cm^{-1}(C=O, ketonic and carboxylic), at 3620-3860 cm^{-1}(phenolic, -OH groups), and at ~3020 cm^{-1} (-CH stretch) shifted to lower absorbance areas indicated that antibiotics sorption had been increased by these functional groups on fBC surface. Raman spectra also confirmed this result. In Raman spectra, the D band indicates the degree of disordered SP^2 hybridization of carbon atom containing vacancies, impurities or defects whereas G band indicates the SP^2 hybridization of carbon atoms in any carbonaceous materials (graphitic carbon). The intensity of the peaks was reduced significantly after sorption of antibiotics. The I_D/I_G ratio also decreased which also confirmed the interactions of antibiotics with the surface functional groups of fBC. The peak intensity decreased due to

sorption of antibiotics by the fBC functional groups leading to blocking the functional groups available for detecting in Raman spectroscopy. This result also confirmed the role of surface disordered structure carbon atoms i.e. D bands at ~1330 cm^{-1} (in the form of oxygenated functional group) while graphitic G-bands at ~1586 cm^{-1} also decreased indicating the role of C=C i.e. π structured carbon atoms. The latter case can be explained by the electron-donar interaction nature of the arene unit in the C=C and C≡C system. Thus Raman spectra indicated the role of functional groups as well as π-π interactions due to change in the peak intensity for G and D bands. In addition, G^* band peak intensity also reduced significantly indicating the π-π interactions. The mechanisms of antibiotic sorption can be also explained based on different pH described below.

The zeta potential value of the fBC was found to be positive at solution pH 1.5 i.e. surface of the fBC gets protonated. Hence, the weak interactions between the opposite charged quadruples might be the main reason for lower sorption of these antibiotics. However, still there was some sorption which can mainly be explained by the EDA interactions. Stronger EDA interaction might be possible when the π-electron depletes any aromatic ring and π-electron rich regions interacts together (Ahmed et al., 2017b). Antibiotics such as SMT, STZ and SMX can act as π-electron-acceptor due to their amino functional groups (donating lone pair electrons to the arene unit) and N and/or O-hetero-aromatic rings (electronic resonance). While CP can also act as π-electron-acceptor site due to its nitro group presence on its arene unit. Moreover, fBC enriched with C=C and C≡C groups along with –OH, C=O and –COOH groups and may act as a strong π-electron-donor or acceptor sites at pH ~1.5. The pK_a values of surface –COOH and surface –OH are ~3.0-5.0 and above 8.0, respectively, hence proton exchange is not possible for those functional groups (Teixidó et al., 2011). However, hydroxyl group in fBC can acts as π-electron donor due to its π-electron donor capacity to the arene unit in fBC, while surface –COOH and –

C=O may act as opposite effect due to its π-electron withdrawal capacity from the arene unit. Hence, at low pH, EDA interactions between –OH groups in fBC and π-electron depleted aromatic unit in antibiotics might be the main sorption mechanism (**Fig. 4**). The π-π electron-acceptor-acceptor (EAA) interactions (due to BC-C=O group and BC-COOH group become electron acceptor as well as antibiotics molecules can behave as electron acceptor site) might also possible but not stronger than EDA interactions (**Fig. 4**). So, at very low pH, competitive sorption of sulfonamides and CP antibiotics on to positively charged fBC were mainly due to EDA interactions and this result is also supported by previous study (Ahmed et al., 2017b; Teixidó et al., 2011).

At pH ~4.0, all sulfonamide antibiotics behaved as neutral species in the solution and CP was more stable. Maximum sorption of all selected antibiotics in competitive mode was found at this pH range. In addition to EDA, strong hydrogen bonds and CAHB formations might be the main sorption mechanisms. As mentioned earlier, the pK_a value of surface –COOH was near ~3.0-5.0, hence, hydrogen bond formations were highly possible among fBC surface –COOH groups and with $–NH_2$ or, $-NO_2$ or hydrogen groups present in sulfonamides and CP antibiotics.

$$\text{Sulfonamides}^0/\text{CP} + H_2O + \text{fBC} = \text{Sulfonamides/CP}^+ \ldots\text{fBC} + OH^- \quad (7)$$

$$\text{Sulfonamides}^0/\text{CP} + \text{fBC} = \text{Sulfonamides/CP}^+ \ldots.\text{fBC}^- \quad (8)$$

$$\text{Sulfonamides}^0 + \text{fBC} = \text{Sulfonamides}^{\pm} \ldots. \text{fBC } (-H^+) \quad (9)$$

$$\text{Sulfonamides}^0 + \text{fBC} = \text{Sulfonamides}^{\pm} \ldots..\text{fBC} + H^+ \quad (10)$$

Proton exchange with water molecule should increase the solution pH by leaving –OH groups in the solution and thus final solution pH should be increased. However, pH shifted to become more acidic indicating that **equation 7** was not the main mechanism (**Fig. 2**), which is consistent with previous studies (Ahmed et al., 2017b, Teixidó et al., 2011). This might be due to the formation of strong H-bond formations for neutral sulfonamides (**equation 8**). The **equation 9** involves

tautomerisation of sulfonamides to the zwitterion in the adsorbed state while **equation 10** shows the tautomerisation by forming the zwitterion and releasing protons in the solution. Thus, the observed equilibrium pH slightly decreased from the initial pH and stabilization of **equations 9 and 10** might be possible through the formation of a π-π EDA which might not be as strong as the positively charged sulfonamide ring system with the biochar surface. Overall stabilization of the cationic form of sulfonamides can be gained through a strong H-bond formation (**Fig. 4**).

On the other hand, CP has a pK_a *v*alue of ~5.50 and thus ΔpK_a for surface –COOH and CP lays ~1.0-1.5. Normally, smaller the difference stronger the hydrogen bond formations (Gilli et al., 2008). More clearly, CP can initially undergo for proton exchange with water molecule and release of –OH in solution (**equation 11**) and the –OH may be neutralize by releasing proton from surface –COOH to form negative CAHB (**equation 12**). This was resulted in slightly decrease in equilibrium pH (**Fig. 2**). Thus at pH ~4.0-4.25, sulfonamides antibiotics molecules mainly formed strong hydrogen bonds whereas CP formed CAHB along with EDA interactions, which were the main reasons for higher sorption of those antibiotics. Moreover, ordinary hydrogen bonds formation among hydrogen in CP and –COOH in fBC might also responsible for the high affinity. The π-π EAA interaction was less effective as biochar surface became negative above pH 2.2 and as surface carboxylate group had pK_a values more than 4.

$$CP + H_2O \rightarrow CP\ldots.H^+ + OH^- \quad (11)$$

$$CP + HOOC\ldots.BC = CP^-\ldots\ldots.H^+\ldots\ldots.^-OOC\text{-}BC + H^+ \quad (12)$$

Lewis acid base electronic interaction might be possible at pH of ~4.0 where sulfonamides remain as a neutral species and thus, loan-pair electrons of amino groups in the arene unit may donate to form a complex with the protonated enriched surface functional groups (Ahmed et al., 2017b).

At pH near 5.5, all the sulfonamide antibiotics remained as minimum ionized states due to intersections points and thus minimum sorption at this pH was found. At the same time, minimum CP sorption was also found (might be just crossing the pK_a matched solution pH). Equilibrium pH moved to ~6.4 also indicating the release of –OH groups in the solution by consuming proton from the solution leading to hydrogen bond formations.

In alkaline solution, the sorption of sulfonamide negative species was found to be significantly lower than for neutral species. This was due to repulsion of negative species sulfonamides as well as negative surface fBC. Teixidó et al. (2011) noted that the adsorption of SMT^- was due to the release of –OH for proton exchange with water molecule ($SMT^- + H_2O \rightarrow SMT^o + OH^-$), followed by interactions of the resulting natural molecules with surface –COOH and –OH groups ($SMT^0 + BC = SMT^0$…..BC). These kinds of bonds formation were designed as strong negative CAHB. They mentioned that pH was raised as SMT^- sorption amount increased. However, in this study it was found equilibrium pH was decreased indicating that protons were released by fBC surface. As the pK_{a2} values of all sulfonamides ranged from 6.16 to 6.99 and pK_a values of phenolic groups ranged from 7 to 10 (Gilli et al., 2008), ΔpK_a value between phenolic groups and sulfonamide groups is around ~0.0-2.5. Thus, initially, sulfonamide antibiotics began with proton exchange with water molecules hence releasing –OH in solution (**equation 13**), followed by neutralization of hydroxyl groups by the release of protons from fBC surface –OH groups through the formation of negative CAHB (**equation 14**).

$$\text{Sulfonamide-N}^- + H_2O \rightarrow \text{Sulfonamide-NH} + OH^- \quad (13)$$

$$\text{Sulfonamide-NH} + \text{HO}\ldots\text{BC} = \text{Sulfonamide-N}^-\ldots.H^+\ldots.^-\text{O-BC}^- + H^+ \quad (14)$$

CP might form CAHB and weak hydrogen bonds among surface hydroxyl groups of fBC, aromatic nitro group and hydroxyl groups (**Fig. 4**). EDA interactions for CP were not favorable at

this pH since the hydroxyl group was deprotonated to form CAHB. In addition, EAA could be possible due to unchanged –COOH groups on fBC surface.

3.5. Treatment of water and synthetic wastewater during competitive removal

Competitive removal of antibiotics was carried out at different dosages of fBC and pronounced differences were observed for lake and synthetic wastewater (**Fig. 5**). In comparison with lake water, synthetic wastewater was found to have more influence on antibiotics removal than lake water. Final lake water TOC value was found to be 46.53 mg L^{-1}.The synthetic wastewater contained different chemicals in the form of inorganic and organic species that could compete with the antibiotics for fBC sorption sites and resulted in lower sorption efficiency with final TOC value of 50.5 mg L^{-1}. Regarding antibiotics themselves, in both water types, STZ sorbed even at 200 mg L^{-1} dosage of fBC while SMT required a higher dosage (~700 mg L^{-1} of fBC, synthetic wastewater) for the complete removal from the mixture solution. Overall, the trend for removing selected antibiotics in competitive mode followed the order of deionized water > lake surface water > synthetic wastewater. Therefore, fBC could be successfully applied for the treatment of a mixture of antibiotics from different water and wastewater.

4. Conclusions

Competitive sorption of sulphonamides and chloramphenicol was very strong toward fBC. Competitive sorption was governed by solution pH and the maximum sorption occurred at pH 4.0-4.25. Sorption affinity decreased in the order STZ < SMX < CP < SMT. fBC was found to be highly efficient in removing these antibiotics from water and wastewater, with the sorption affinity following the order of deionized water > lake water > synthetic wastewater. The sorptive mechanisms were addressed in detail based on resonance effect of arene units. The results

demonstrate that fBC is very effective in removing antibiotics mixture from water and wastewater.

5. Supplementary information

Physicochemical properties of the antibiotics (Table A1), summary of the kinetic model parameters for antibiotics sorption on fBC (Table A2), EDS data for fBC (Table A3), FTIR and Raman spectra of fBC before and after sorption (Fig. A1), possible resonance structures of antibiotics and fBC and their electron donor and acceptor sites (Fig. A2).

6. Acknowledgements

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References

1. Ahmed M.B., Zhou J.L., Ngo H.H., Guo W.S., 2015. Adsorptive removal of antibiotics from water and wastewater: Progress and challenges. Sci. Total Environ. 532, 112-126.
2. Ahmed M.B., Zhou J.L., Ngo H.H., Guo W.S., Chen M., 2016a. Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. Bioresour. Technol. 214, 836-851.
3. Ahmed M.B., Zhou J.L., Ngo H.H., Guo W.S., 2016b. Insight into biochar properties and its cost analysis. Biomass Bioenerg. 84, 76-86.

4. Ahmed M.B., Zhou J.L., Ngo H.H., Guo W.S., Thomaidis N.S., Xu J., 2017a. Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review. J. Hazard. Mater. 323, 274-298.

5. Ahmed M.B., Zhou J.L., Ngo H.H., Guo W.S., Johir M.A.H., Sornalingam K., 2017b. Single and competitive sorption properties and mechanism of functionalized biochar for removing sulfonamide antibiotics from water. Chem. Eng. J. 311, 348-358.

6. Azhar M.R., Abid H.R., Sun H., Periasamy V., Tadé M.O., Wang S., 2016. Excellent performance of copper based metal organic framework in adsorptive removal of toxic sulfonamide antibiotics from wastewater. J. Colloid Interface Sci. 478, 344-352.

7. Carvalho I.T. and Santos L., 2016. Antibiotics in the aquatic environments: a review of the European scenario. Environ. In. 94, 736-757.

8. Calisto V., Jaria G., Silva C.P., Ferreira C.I., Otero M., Esteves V.I., 2017. Single and multi-component adsorption of psychiatric pharmaceuticals onto alternative and commercial carbons. J. Environ. Manag. 192, 15-24.

9. Chen, D., Yu, X., Song, C., Pang, X., Huang, J., Li, Y., 2016. Effect of pyrolysis temperature on the chemical oxidation stability of bamboo biochar. Bioresour. Technol. 218, 1303-1306.

10. Cui, E., Wu, Y., Zuo, Y., Chen, H. 2016. Effect of different biochars on antibiotic resistance genes and bacterial community during chicken manure composting. Bioresour. Technol. 203, 11-17.

11. Devi, P., Saroha, A.K., 2014. Synthesis of the magnetic biochar composites for use as an adsorbent for the removal of pentachlorophenol from the effluent. Bioresour. Technol. 169, 525–531.

12. Fukahori, S., Fujiwara, T., Ito, R., Funamizu, N., 2011. pH-dependent adsorption of sulfa drugs on high silica zeolite: modeling and kinetic study. Desalination 275, 237-242.

417 13. Gilli P., Pretto L., Bertolasi V., Gilli G., 2008. Predicting Hydrogen-Bond Strengths from
418 Acid− Base Molecular Properties. The pKa Slide Rule: Toward the Solution of a Long-
419 Lasting Problem. Acc. Chem. Res. 42, 33-44.
420 14. Grover D., Zhou, J.L., Frickers, P.E., Readman, J.W., 2011. Improved removal of estrogenic
421 and pharmaceutical compounds in sewage effluent by full scale granular activated carbon:
422 impact on receiving river water. J. Hazard. Mater. 185, 1005-1011.
423 15. Lian F., Sun B., Song Z., Zhu L., Qi X., Xing B., 2014. Physicochemical properties of herb-
424 residue biochar and its sorption to ionizable antibiotic sulfamethoxazole. Chem. Eng. J. 248,
425 128-134.
426 16. Nielsen L. and Bandosz T.J., 2016. Analysis of the competitive adsorption of pharmaceuticals
427 on waste derived materials. Chem. Eng. J. 287, 139-147.
428 17. Maskaoui K. and Zhou J.L., 2010. Colloids as a sink for certain pharmaceutical in the aquatic
429 environment. Environ. Sci. Pollut. Res. 17, 898-907.
430 18. Pavlović D.M., Ćurković L., Blažek D., Župan J., 2014. The sorption of sulfamethazine on
431 soil samples: Isotherms and error analysis. Sci. Total Environ. 497, 543-552.
432 10. Pei, Z., Yang, S., Li, L., Li, C., Zhang, S., Shan, X. Q., Wen, B., Guo, B., 2014. Effects of
433 copper and aluminum on the adsorption of sulfathiazole and tylosin on peat and soil.
434 Environ. Pollut. 184, 579-585.
435 20. Rajapaksha, A.U., Vithanage, M., Zhang, M., Ahmad, M., Mohan, D., Chang, S.X., Ok, Y.S.,
436 2014. Pyrolysis condition affected sulfamethazine sorption by tea waste biochars. Bioresour.
437 Technol. 166, 303–308.
438 21. Seifrtová M., Nováková L., Lino C., Pena A., Solich P., 2009. An overview of analytical
439 methodologies for the determination of antibiotics in environmental waters. Anal. Chim.
440 Acta 649, 158-179.

441 22. Tang, J., Lv, H., Gong, Y., Huang, Y., 2015. Preparation and characterization of a novel
442 graphene/biochar composite for aqueous phenanthrene and mercury removal. Bioresour.
443 Technol. 196, 355–363
444 23. Teixidó M., Pignatello J.J., Beltrán J.L., Granados M., Peccia J., 2011. Speciation of the
445 ionizable antibiotic sulfamethazine on black carbon (biochar). Environ. Sci. Technol. 45,
446 10020-10027.
447 24. Veksha, A., McLaughlin, H., Layzell, D. B., Hill, J. M., 2014. Pyrolysis of wood to biochar:
448 Increasing yield while maintaining microporosity. Bioresour. Technol. 153, 173-179.
449 25. Wang, B., Jiang, Y. S., Li, F. Y., Yang, D. Y. 2017. Preparation of biochar by simultaneous
450 carbonization, magnetization and activation for norfloxacin removal in water. Bioresour.
451 Technol. 233, 159-165.
452 26. Wang, F., Ren, X., Sun, H., Ma, L., Zhu, H., Xu, J., 2016. Sorption of polychlorinated
453 biphenyls onto biochars derived from corn straw and the effect of propranolol. Bioresour.
454 Technol. 219, 458-465.
455 27. Xie A., Dai J., Chen X., Zou T., He J., Chang Z., Li C., Yan Y., 2016. Hollow imprinted
456 polymer nanorods with a tunable shell using halloysite nanotubes as a sacrificial template for
457 selective recognition and separation of chloramphenicol. RSC Adv. 6, 51014-51023
458 28. Xie M., Chen W., Xu Z., Zheng S., Zhu D., 2014. Adsorption of sulfonamides to
459 demineralized pine wood biochars prepared under different thermochemical conditions.
460 Environ. Pollut. 186, 187-194.
461 29. Yao Y., Gao B., Chen H., Jiang L., Inyang M., Zimmerman A.R., Cao X., Yang L., Xue Y.,
462 Li H., 2012. Adsorption of sulfamethoxazole on biochar and its impact on reclaimed water
463 irrigation. J. Hazard. Mater. 209, 408-413.

464 30. Yu F., Li Y., Han S., Ma J., 2016. Adsorptive removal of antibiotics from aqueous solution
465 using carbon materials. Chemosphere 153, 365-385.
466 31. Zhao H., Liu X., Cao Z., Zhan Y., Shi X.,. Yang Y, Zhou J., Xu J., 2016. Adsorption
467 behavior and mechanism of chloramphenicols, sulfonamides, and non-antibiotic
468 pharmaceuticals on multi-walled carbon nanotubes. J. Hazard. Mater. 310, 235-245.
469 32. Zheng H., Wang Z., Zhao J., Herbert S., Xing B., 2013. Sorption of antibiotic
470 sulfamethoxazole varies with biochars produced at different temperatures. Environ. Pollut.
471 181, 60-67.

Figure captions

Fig. 1. Effect of pH on K_d (with standard deviation) during the removal of sulfonamides and chloramphenicol antibiotics using fBC (80 mg L^{-1}) with initial individual antibiotic concentration of 1.0 mg L^{-1} at 25 ^{o}C (a). Competitive sorption kinetics data with PSO and PFO model fitting using 1.0 mg L^{-1} initial antibiotics concentration and 80 mg L^{-1} of fBC at pH 4.0- 4.25 (b).

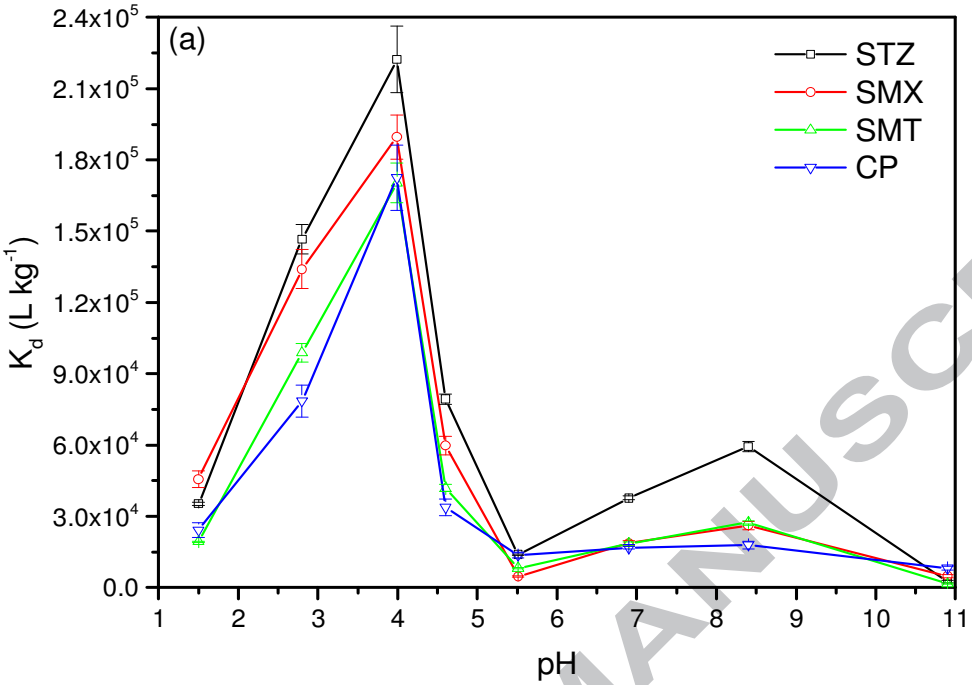
Fig. 2. Zeta potential values of fBC and pH shift during pH effect study.

Fig. 3. Sorption isotherm plots and model fitting for mixtures of antibiotics (initial concentration of each antibiotic was 0.250-20.0 mg L^{-1}) at pH 4.0-4.25 using fBC dosage of 80 mg L^{-1}.

Fig. 4. Proposed sorption mechanisms for the removal of antibiotics in competitive mode using fBC.

Fig. 5. Sorption of antibiotics (%) in mixture mode with 1.0 mg L^{-1} initial concentration of each antibiotic from lake water (a) and synthetic wastewater (b) with different dosages of fBC at pH 4.0-4.25 and 25 ^{o}C.

491 **Fig. 1.**



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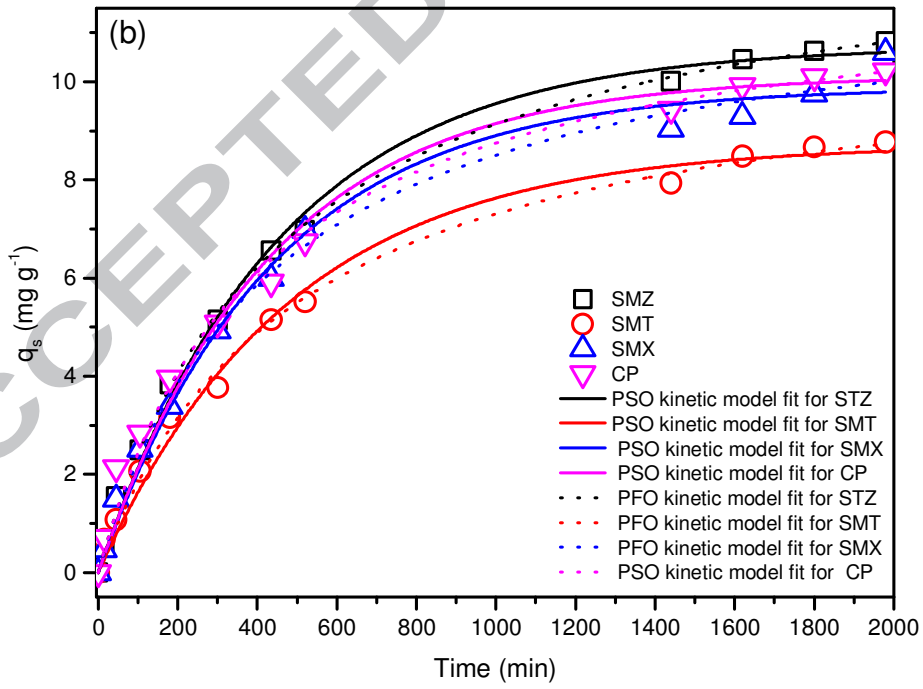

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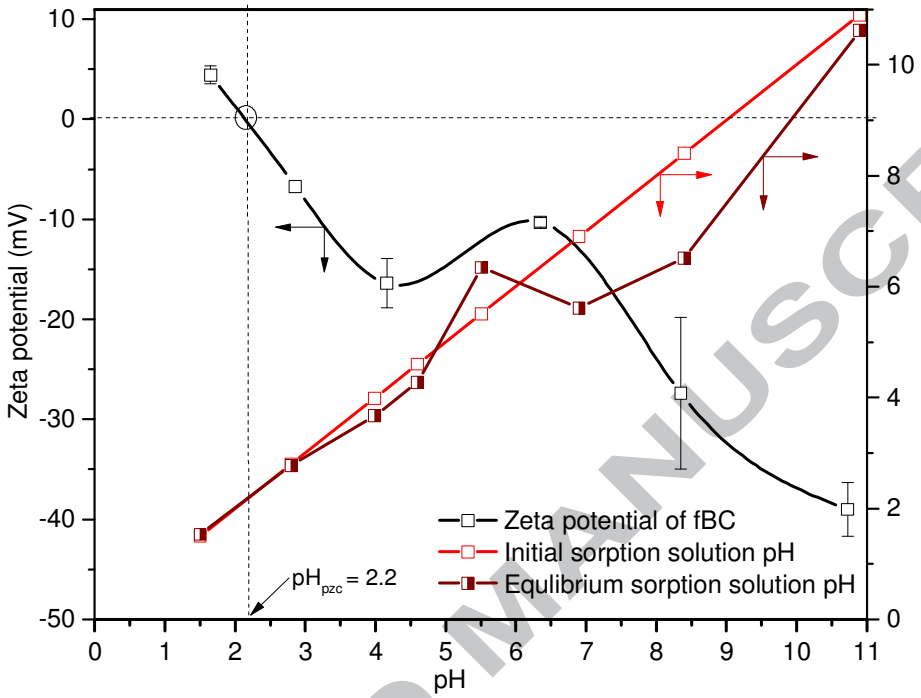
495 **Fig. 2.**



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498 **Fig. 3.**

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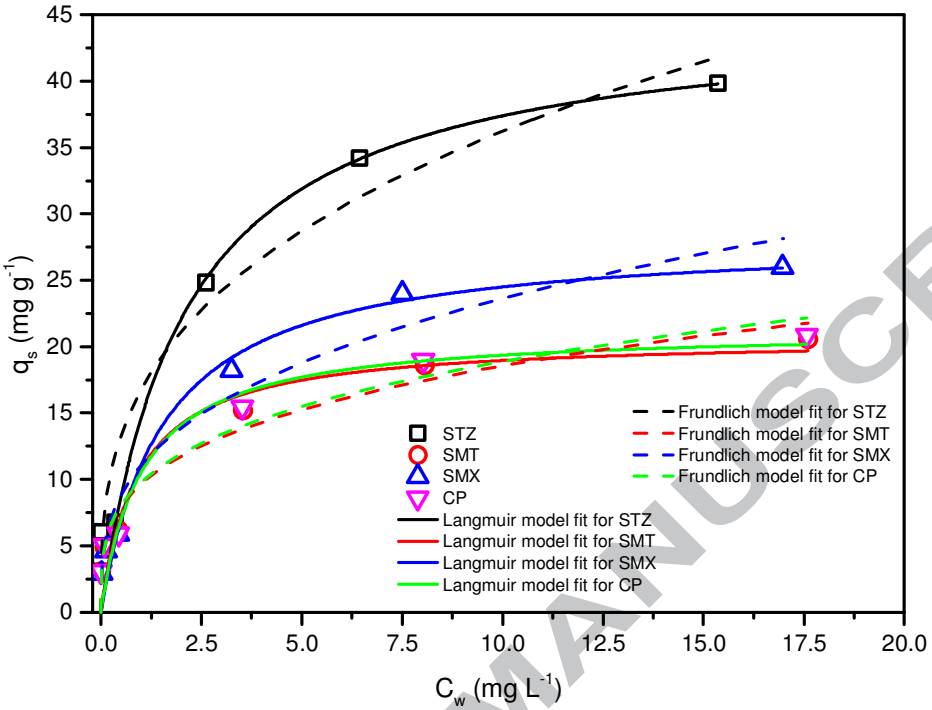

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501 **Fig. 4.**

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Competitive Sorption Affinity Mechanisms

At very low pH:
(i). Repulsion interactions
(ii). BC-OH + sulfonamides/CP = EDA interactions

At pH 4.0-4.25:
(i). BC-COO^-.....H^+....^-O_2N-chloramphenicol = CAHB formations with EDA interactions
(ii). BC-COO..H + sulfonamides ($NHSO_2$-/NH/ -NH_2/CH_3) = H-bond formations

At pH above 7.0:
(i). Repulsion interactions
(ii). Sulfonamides-N^- + H_2O = sulfonamides-NH + -OH^+
(iii). BC-O....H + $^-$N....sulfonamides =BC-O^-.....H^+....$^-$N..sulfonamides = CAHB
(iv). BC-OH + chloramphenicol (H^+/-OH/NO_2/-NH-/-Cl) = H-bond formations

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507 **Fig. 5.**
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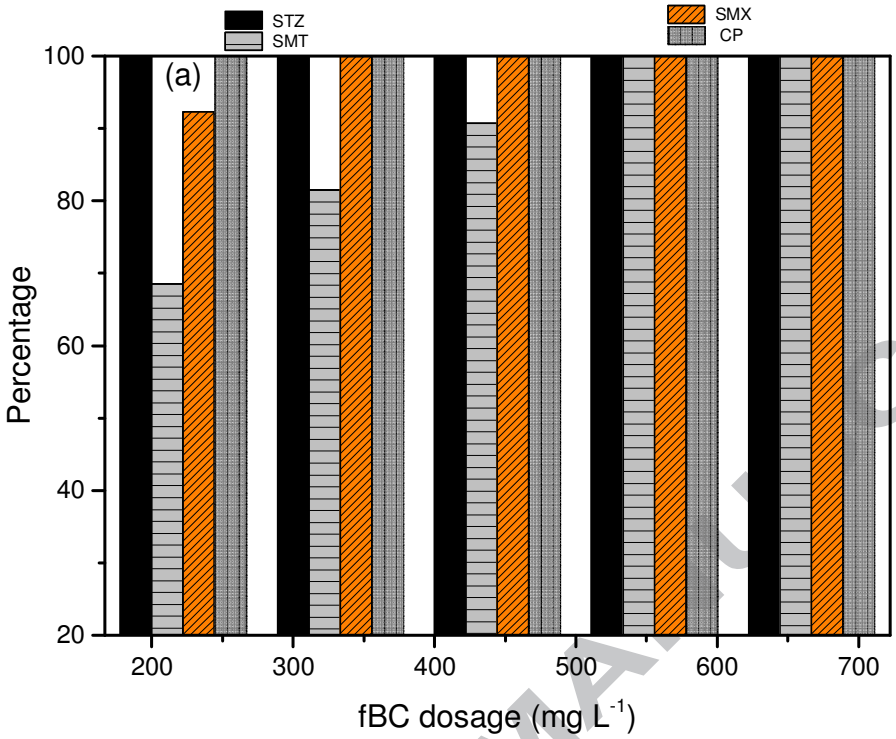

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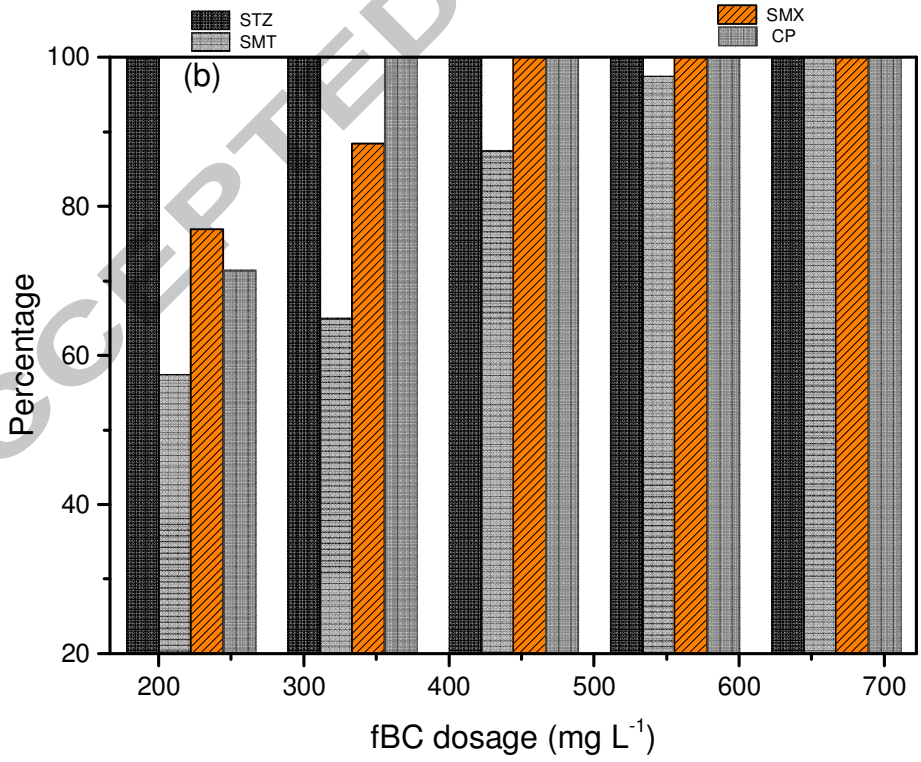

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512

513 **Table 1.** Summary of the Freundlich and Langmuir isotherm parameters for competitive

514 antibiotic sorption on fBC at 25 ± 0.5 °C.

	Freundlich isotherm parameters			Langmuir isotherm parameters		
Antibiotic	K_F	n	R^2	q_{max}	K_L	R^2
STZ	16.76±2.53	2.99±0.60	0.942	45.19±5.03	0.48±0.20	0.956
SMT	9.65±1.21	3.52±0.67	0.930	20.71±1.99	1.08±0.54	0.915
SMX	11.04±1.33	3.03±0.47	0.949	28.29±2.30	0.65±0.23	0.965
CP	9.81±1.28	3.52±0.70	0.925	21.35±2.27	0.97±0.52	0.906

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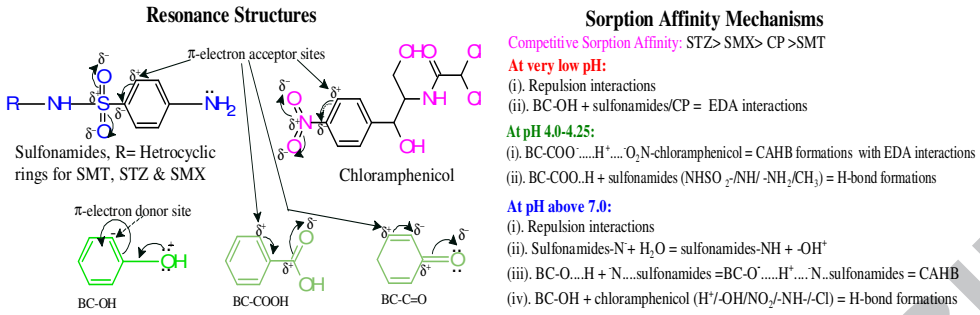
518 **Graphical abstract**



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523 **Highlights**

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525 ❖ Competitive sorption affinities followed the order: STZ > SMX > CP > SMT.

526 ❖ Maximum sorption affinity was found at pH ~4.0-4.25 for all antibiotics.

527 ❖ Main sorption mechanisms were H-bonds and charge assisted hydrogen bond formation.

528 ❖ Electron-donor-acceptor interactions also played a significant role.

529 ❖ Sorption decreased as deionized water > lake water > synthetic wastewater.

530