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WATER: FROM POLLUTION TO PURIFICATION

Effect of hydrophobicity of pharmaceuticals and personal care products for adsorption on activated carbon: Adsorption isotherms, kinetics and mechanism

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Abstract Adsorption of three pharmaceuticals and personal care products (PPCPs), namely caffeine, ibuprofen and triclosan on commercial powdered activated carbon was examined in aqueous medium. The contaminants were chosen based on their diverse log K_{ow} (octanol-water partition coefficient) viz. − 0.07 for caffeine, 3.97 for ibuprofen and 4.76 for triclosan to examine the role of hydrophobicity on adsorption process. The adsorbent characterisation was achieved using BET surface area, SEM, pore size distribution studies and FTIR. Influence of mass of PAC, contact time, solution pH and initial concentration on adsorption capacity of PAC was studied. Adsorption isotherms and kinetics were applied to establish the mechanism of adsorption. The kinetics followed pseudo-second order with physisorption occurring through particle diffusion. The Freundlich model fitted best among the isotherm models. The adsorption capacity increased in the order CFN < IBU < TCS which correlates with increasing hydrophobicity (log K_{ow}), molecular weight and decreasing water solubility, respectively. We conclude that micro-pollutant hydrophobicity contributes towards adsorption on activated carbon.

Keywords PPCPs · Water pollution · Removal · Powdered activated carbon · Hydrophobicity

Introduction

Pharmaceuticals and personal care products (PPCPs) are detected in water matrices worldwide (Ferreira et al. 2015; Lim et al. 2017). The diverse physicochemical properties of PPCPs, occurrence at concentrations as low as parts per trillion and bioaccumulation potential poses challenge towards their removal from water. The tendency for contaminants to accumulate in biological tissues accounts for their persistence and fate in water bodies (Seo et al. 2016). It is expressed in terms of octanol-water partition coefficient (log K_{ow}). Contaminants with log $K_{ow} < 3$ or less hydrophobic possess low bioaccumulation potential, those with log $K_{ow} \geq 3$ but ≤ 4 i.e. moderately hydrophobic possess moderate bioaccumulation and those with log $K_{ow} > 4$ i.e. highly hydrophobic are believed to have significant potential for bioaccumulation (Grassi et al. 2012; Nam et al. 2014; Chang et al. 2015; Dhillon et al. 2015).

It has been well established that micro-pollutant adsorption on activated carbon is greatly influenced by their molecular size, hydrophobicity (represented by log K_{ow}), charge, etc. (Hamdaoui and Neffrechoux 2007; Rattier et al. 2012; Sheng et al. 2016; Zhu et al. 2016). The molecule's solubility is another important property affecting the adsorption process. High water solubility impedes molecule's affinity towards the adsorbent surface (Ngeno et al. 2016). Among targeted contaminants, caffeine, a common stimulant encountered in water and wastewater is used as an anthropogenic marker. It is highly soluble in water (solubility 21,600 mg L^{-1}) and has low bioaccumulation potential (log K_{ow} − 0.07). In a recent study conducted by Anumol et al. (2016) in Chennai (India), caffeine was the most commonly detected trace organic contaminant (TrOC) in the WWTP influents under study. Ibuprofen is a non-steroidal anti-inflammatory drug (NSAID) widely consumed worldwide. It is moderately soluble in water (solubility 21 mg L^{-1}) and has potential for bioaccumulation (log K_{ow} 3.97). Shanmugam

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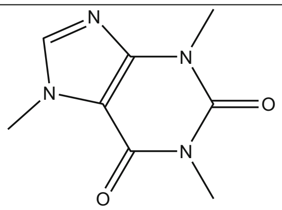
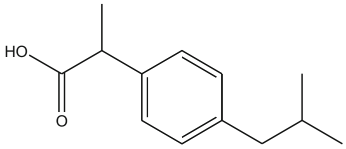
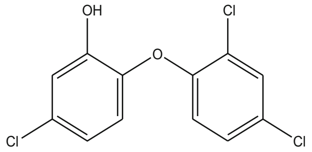
Table 1 Physicochemical properties of three selected micro-pollutants under study

Micro-pollutant	Molecular mass	Molecular size (nm)	Log K_{ow}	Water solubility (mg L^{-1})	Common usage	Structure
Caffeine	194.2	$0.98 \times 0.87 \times 0.56^{a}$	−0.07	21,600	Stimulant	
Ibuprofen	206.3	$1.06 \times 0.57 \times 0.46^{b}$	3.97	21	Non-steroidal anti-inflammatory drug (NSAID)	
Triclosan	289.5	$1.42 \times 0.69 \times 0.75^{c}$	4.76	10	Antimicrobial agent	

[a] Alvarez-Torrellaz et al. 2016

[b] Gonzales et al. 2013

[c] Nghiem and Coleman 2008

et al. (2014) studied the occurrence of NSAIDs in Indian rivers and reported ibuprofen as the second most frequently detected pharmaceutical. Triclosan is an antimicrobial component in personal care products such as toothpaste, soaps etc. It is poorly soluble in water (solubility 10 mg L^{-1}) and has significant bioaccumulation potential (log K_{ow} 4.76) owing to which its removal by adsorption in aqueous medium is feasible (Weiner et al. 2017). Ramaswamy et al. (2011) have reported triclosan in Tamiraparani River of Tamil Nadu (India) which is among the highest concentration detected in surface water in India.

Activated carbons (ACs) have proven to substantially remove organic contaminants from water even at low concentrations (Fierro and Torne 2008; Redding et al. 2009). This may be attributed to their high specific surface area which lies typically in the range 500–1400 m^2 g^{-1} with large pores (mesopores; $r = 20$–500 Å, macropores; $r > 500$ Å) and small pores (micropores; $r < 20$ Å) (Hesas et al. 2013). Adsorption does not augment undesirable by-products (Tong et al. 2010). Apart from activated carbon, various other adsorbents have been studied for adsorptions of PPCPs. Zhou et al. (2013) studied triclosan adsorption on multi-walled carbon nanotubes (MWCNTs) under different solution conditions. However, they also mentioned that the risk to environment caused by MWCNTs cannot be neglected. Tong et al. (2016) have reported biochar derived from

Table 2 Kinetic models and parameters for PPCPs adsorption on activated carbon

Kinetic model	Kinetic parameters	Basic features
Pseudo-first order (PFO; Lagergren) *Linear form:* $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	k_1 (min^{-1}): rate constant of pseudo-first order reaction.	Plot of $\log(q_e - q_t)$ versus t gives rate constant k_1.
Pseudo-second order (PSO) *Linear form* $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2 (g mg^{-1} min^{-1}): rate constant for pseudo-second order. $k_2 q_e^2 = h$ (mg g^{-1} min^{-1}): Initial sorption rate.	Used to calculate kinetic parameters; k_2, q_e and h
Particle diffusion (PDM) *Linear form* $\ln C_t / C_e = -k_p t$	k_p (mg g^{-1} min^{-1}): particle diffusion coefficient.	Particle diffusion is the rate determining step if straight line is obtained on plotting $\ln C_t/C_e$ versus t.
Intra-particle diffusion (IPDM): *Linear form* $q_t = k_{int} t^{1/2} + c$	k_{int} (mg g^{-1} $min^{-0.5}$): intra-particle diffusion rate constant. c:constant related to thickness of boundary layer.	Pore diffusion is the rate determining step if straight line is obtained passing through origin on plotting q_t versus $t^{1/2}$.

Table 3 Isotherm models and parameters for PPCPs adsorption on activated carbon

Isotherm model	Isothermal parameters	Basic features
Freundlich *Linear form:* $logq_e = \log K_f + \frac{1}{n} logC_e$ Knowing K_f and 1/n from above equation, q_m may be calculated: $K_f = \frac{q_m}{(C_0)^{1/n}}$	q_e(mg g^{-1}): amount of solute adsorbed per unit weight of adsorbent at equilibrium. K_f (mg $L^{1/n}$/g mg $^{1/n}$): Freundlich constant *n*: empirical parameter related to heterogeneity of adsorption sites ($0 < 1/n < 1$) q_m (mg g^{-1}): Freundlich maximum adsorption capacity	Adsorption is multilayer, occurs mostly on heterogeneous surfaces.
Langmuir *Linear form:* $\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}$	K_L (dm^3 mg^{-1}): adsorption energy q_m (mg g^{-1}): monolayer adsorption capacity. R_L: measure of adsorption efficiency $R_L = \frac{1}{1+K_L C_0}$ Adsorption irreversible: $R_L = 0$, Favourable: $0 < R_L < 1$, Linear: $R_L = 1$, unfavourable: $R_L > 1$	Monolayer adsorption onto homogenous surface with sites of identical nature.
D-R (Dubinin-Radushkevish) *Linear form* $\ln q_e = \ln q_m - \beta\varepsilon^2$ where $E = \frac{1}{\sqrt{2\beta}}$	β (mo ^{2} J^{-2}): activity coefficient constant related to sorption energy. ε: Polanyi potential. *E* (KJ mol^{-1}): mean free sorption energy per molecule of sorbate. $E < 8$: physisorption, $E > 8$: chemisorption $8 < E < 16$: adsorption through chemical ion exchange	To differentiate physisorption and chemisorption through mean free adsorption energy.

biosolids for triclosan removal from wastewater effluent. Additionally, they proposed the need to study comparative adsorption of compounds differing in their hydrophobicity.

Darco G60 is a commercial activated carbon used specifically for pharmaceutical adsorption. It possesses certain characteristic properties such as its high purity, pH range 6–8 which is relevant to water and wastewater streams. Members of the Darco grades are known for exceptionally high adsorption capacity. Additionally, the adsorbent is not known to pose any environmental risk. Unlike other common carbonaceous materials such as Norit, Filtrasorb (F200, F400, etc.), the potential of this carbon has not been extensively studied for micro-pollutant removal. Though, the adsorbent has been studied for trace organic contaminants such as pesticides e.g. diuron and bromoxylin (Yang et al. 2004), a detailed study on its adsorption behaviour towards the targeted PPCPs has not been reported. Hence, this study will serve as benchmark for future applications.

In this study, the behaviour of PPCPs differing in their log K_{ow} and solubility in water was investigated towards adsorption on commercial powdered activated carbon (Darco G 60) in water. The high solubility of caffeine (21,600 mg L^{-1}) implies its higher affinity for water. It was thus hypothesised that caffeine would be less effectively adsorbed than the other two micro-pollutants which are substantially less hydrophilic or more hydrophobic and less water soluble. The adsorption conditions were optimised to attain substantial removal of the contaminants under study.

Table 4 Textural parameters of Commercial PAC (Darco G 60)

Surface area (m^2 g^{-1})		Pore volume (cm^3 g^{-1})			Pore diameter (Å)
S_{BET}	S_{mic}	V_{total}	V_{mic}	V_{meso}	D_p
882.63	671.11	0.67	0.29	0.38	30.725

Materials and methods

Adsorbent

Commercial activated carbon (Darco G60) was purchased from Sigma-Aldrich (India). The carbon was washed thoroughly using ultrapure water, oven dried for 24 h and kept at 60 °C before use. The activated carbon was further characterised using Nitrogen adsorption isotherm for Brunauer, Emmett and Teller surface area (BETSA), Fourier Transform Infra-red spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM). BET surface area measurement and pore size distribution studies were conducted using Micromeritics ASAP 2020 at − 196.137 °C. Standard Harkins & Jura method was used to calculate pore volume. The SEM studies were conducted on JEOL SEM (JSM – IT300) instrument at a working distance of 10.9 mm and working potential difference of 15.0 kV. Micrographs were obtained at various bar lengths ranging from 1 to 50 μm with 1000–10,000x magnifications. FTIR analysis was done using Vertex-70 FTIR (Bruker, Germany). The spectra were studied from 400 to 4000 cm^{-1} range with 4 cm^{-1} resolution and 16 scans.

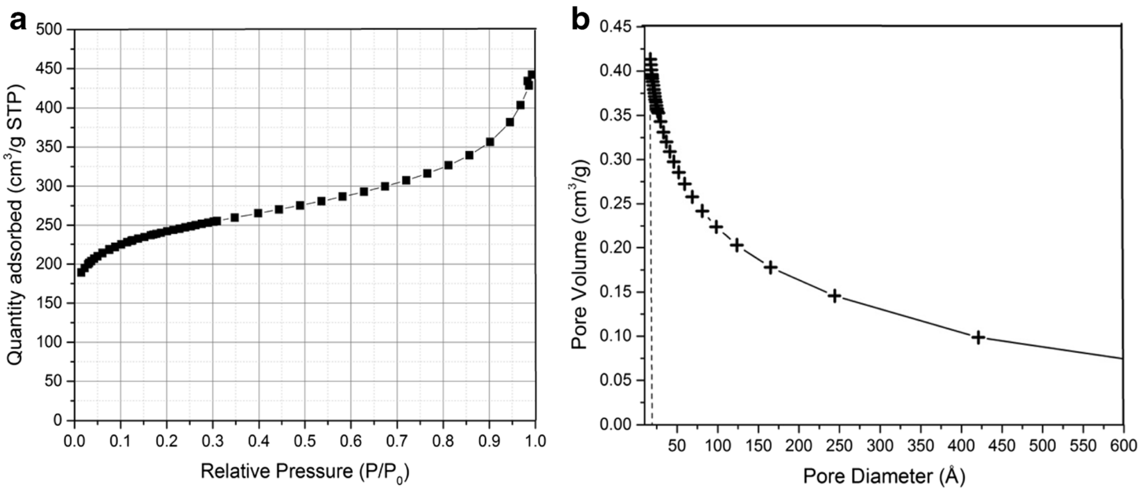


Fig. 1 Nitrogen adsorption isotherm (**a**) and pore size distribution (**b**) of activated carbon Darco G 60

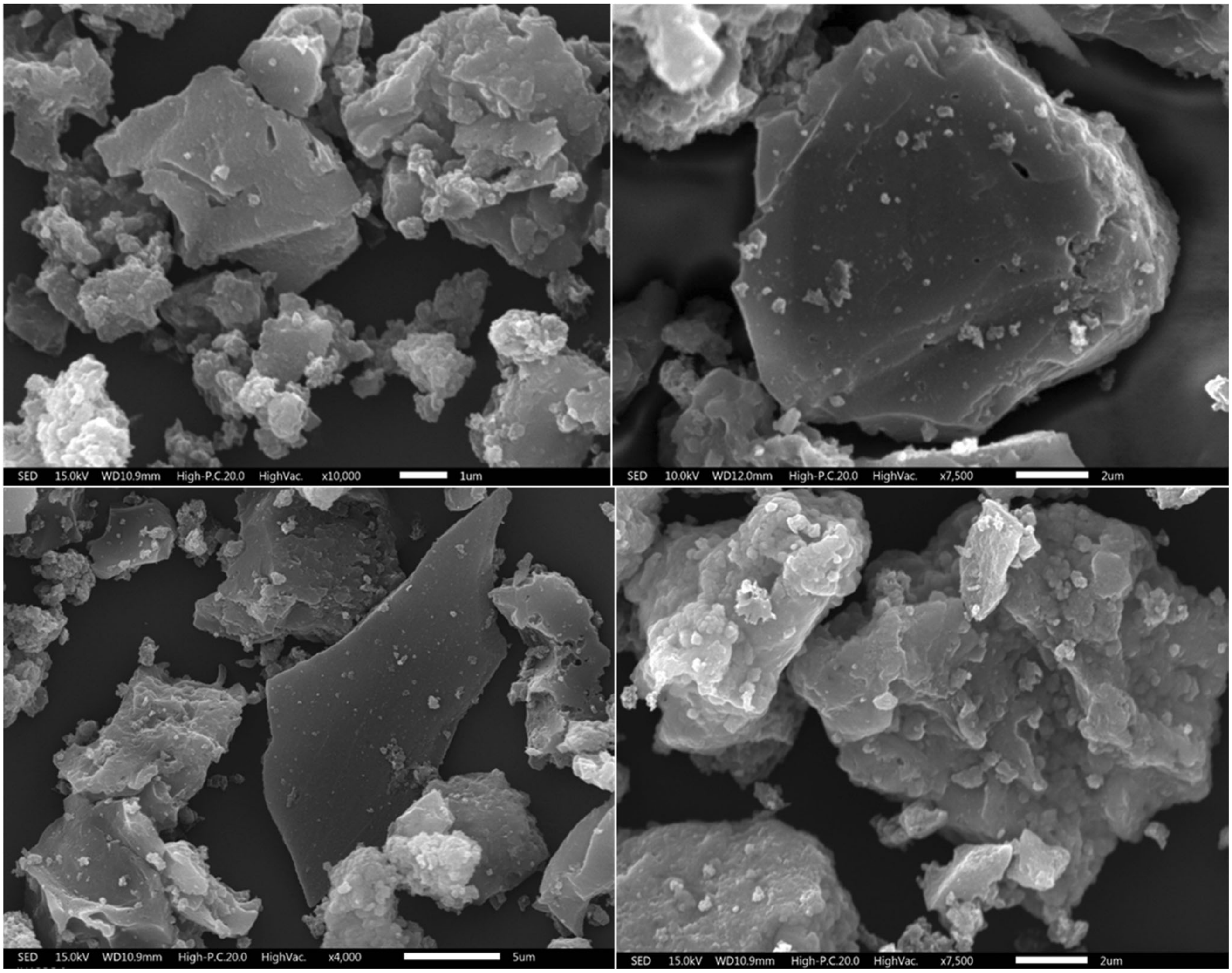


Fig. 2 Scanning electron micrographs of activated carbon

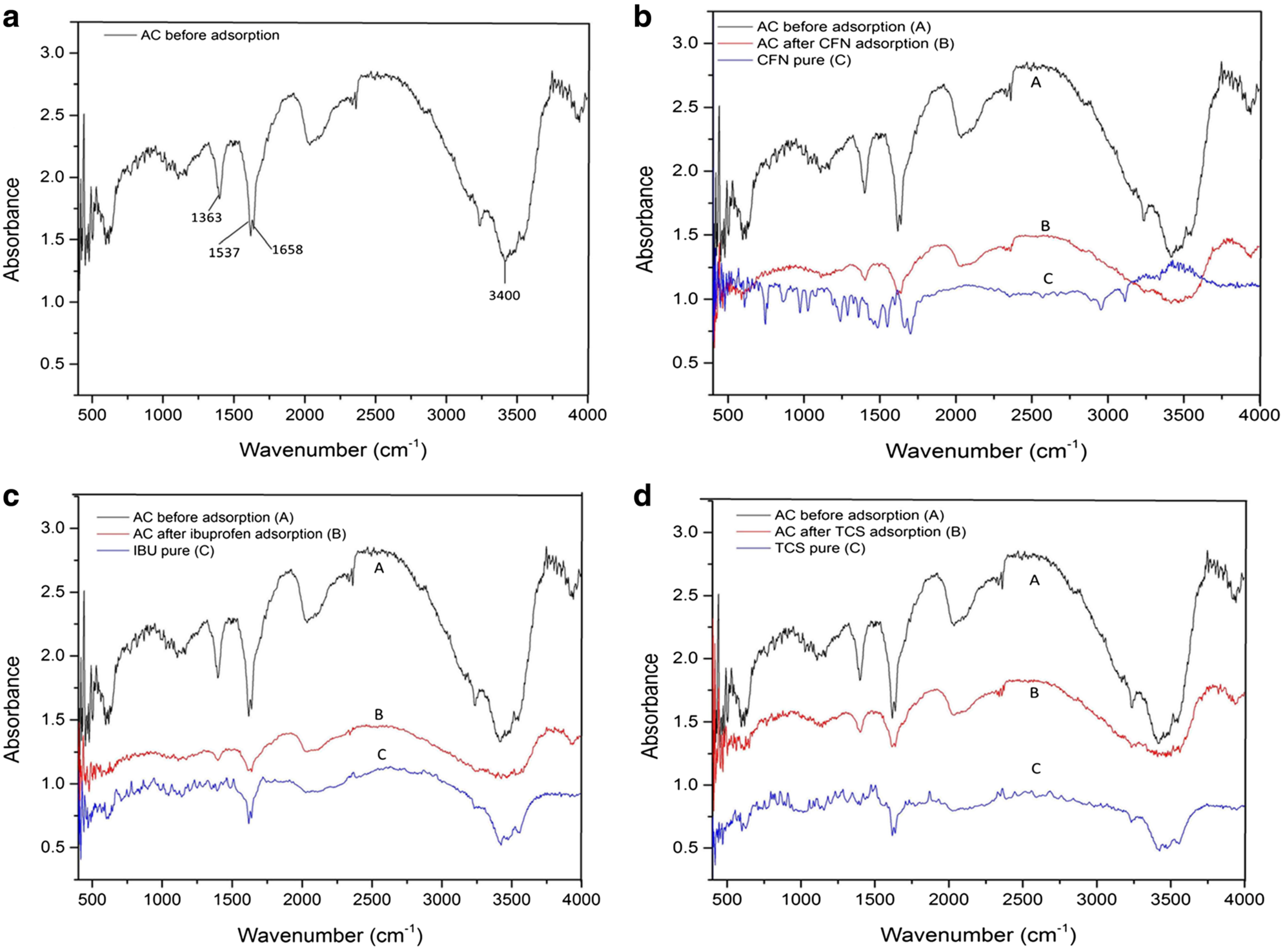


Fig. 3 FTIR spectra of **a** powdered activated carbon (PAC), **b** pure caffeine (CFN) and caffeine adsorbed activated carbon, **c** pure ibuprofen (IBU) and ibuprofen-adsorbed carbon, **d** pure triclosan (TCS) and triclosan-adsorbed carbon

Adsorbates

Caffeine (≥ 99.9%) was purchased from Merck (India), triclosan (≥ 99.9%) and Ibuprofen (≥ 98%) were purchased from Sigma-Aldrich (India). Ten milligrams of micro-pollutant was dissolved in 10 ml of solvent (methanol for caffeine and triclosan and acetonitrile for ibuprofen) to prepare stock solution. All working solutions were prepared in ultrapure water (resistivity 18 MΩ). A volume of 100 cm^3 was used in all adsorption studies. The physicochemical properties of the selected PPCPs are given in Table 1.

Instrumental method

All chemicals (methanol, acetonitrile, ammonium acetate, phosphoric acid) used were of HPLC grade. The target compounds were analysed using Dionex Ultimate 3000 UHPLC-PDA (Thermo Scientific) with Agilent RRHD Eclipse plus C_8 column. The instrument conditions were optimised to obtain linearity, precision and accuracy. The calibration standards were prepared in mobile phase based on solubility of each micro-pollutant. Stock solutions of caffeine and triclosan were prepared in methanol while that of ibuprofen in acetonitrile. Working standards were prepared in the range 0.3125–10 mg L^{-1} to obtain correlation coefficient of ≥ 0.999 for each calibration. Caffeine was analysed at 272 nm using mobile phase water:methanol (60:40), ibuprofen at 224 nm using 10 mM ammonium acetate:acetonitrile (70:30) and triclosan at 280 nm (Liu et al. 2012) using 10 mM phosphate buffer (pH 3):methanol (28:72).

pH study

The pH drift method was used to deduce pH at point of zero charge (pH_{pzc}) and procedure followed as reported by Putra et al. (2009) and Peña et al. (2012). The experiment was conducted by using 0.15 g of activated carbon in 50 cm^3 of 0.01 N NaCl was prepared and pH adjusted between 3 and 8 by 0.1 N HCl and 0.1 N NaOH. The pH was checked after a period of 48 h using WTW Inolab pH 720 pH meter.

Table 5 Major peaks in FTIR spectrum of adsorbent and micro-pollutants

Compound	Peak position (cm^{-1})	Bond assignment
AC (Darco G 60)	1363.61 1536.04	N–O stretch
	1628.05 1658.87	C=C (aromatic ring)
CFN (after adsorption)	1369.24	C–N
	1658.26	C=O
	1726.51	C=C (cyclic hydrocarbons)
	2955.86	CH_3 stretching
	3112.68	C–H (aromatic)
IBU (after adsorption)	1597.84	C=C (aromatic)
	1696.34	C=O
	2364.17	C–H bend (aromatic)
	3404	OH (COOH)
TCS (after adsorption)	720.29, 797.33	C–Cl
	1179.31, 1229.77	C–O–C stretch (diaryl)
	1367.17	OH (phenolic)
	1661.03	C=O
	1728.71	C=C (cyclic hydrocarbons)
	1988.23	C–H bend (aromatic)

Adsorption modelling

Kinetic modelling Batch adsorption experiments were conducted using orbital shaking incubator (make: Remi) at 120 rpm for 4 h and 30 ± 2 °C. A 100 cm^3 volume of 1 mg L^{-1} aqueous solution of caffeine, ibuprofen and triclosan was used for adsorption by a minimum dose of 10 mg L^{-1} activated carbon. Control experiments were performed without Darco G 60. Samples were filtered using 0.22 μm Agilent syringe filters prior to injection into UHPLC. Contaminant amount adsorbed was calculated using Eq. (1):

$$q_t = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_t (mg g^{-1}) is the adsorbate (micro-pollutant) quantity adsorbed onto carbon at a time (t), C_o (mg dm^3) is adsorbate initial concentration, C_e (mg dm^3) is the adsorbate final concentration, V (dm^3) is the volume of adsorbate (micro-pollutant) solution, and m (g) is the adsorbent mass. The adsorption efficiency (%) was calculated using Eq. (2) as mentioned below:

$$\%removal = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Both pseudo-first order (PFO) as well as pseudo-second order (PSO) kinetics were applied on the adsorption data. Since, adsorption could also occur via diffusion between or through the pores of the carbon, both particle diffusion model (PDM) and intra-particle pore diffusion model (IPDM); Webber and Morris were used to determine adsorption mechanism. The kinetic equations used to fit the data are presented in Table 2:

Isotherm modelling Three isotherm models viz. Freundlich, Langmuir and D-R (Dubinin-Radushkevish) as shown in Table 3 were fitted on the adsorption data to study adsorption capacity and mechanism (Suteu and Malutan 2013; Kamau and Kamau 2017).

Results and discussion

Adsorbent characterisation

The BET surface area (S_{BET}), total pore volume (V_t), micropore volume (V_{mic}) and average pore diameter (D_p) obtained by applying BET equation at − 196.137 °C are shown in Table 4. The total pore volume was calculated at the relative partial pressure (P/P_o) of 0.9922. The total pore volume (V_t) and micropore volume (V_{mic}) were considered while calculating the mesoporous volume (V_{meso}) (Fig. 1). As per IUPAC classification for dimensions of pore size, micropores have pore size < 20 Å, mesopores have pore size between 20 and 500 Å and macropores have pore size > 500 Å. The pore size distribution studies revealed that the activated carbon comprised largely of mesopores and some micropores. Thus, the adsorbent was found to be of mesoporous nature.

SEM micrographs of the activated carbon presented in Fig. 2 show local and near surface structures with aggregated irregular surfaces comprising pores and crevices of various sizes.

The FTIR spectra of the adsorbent before and adsorption of micro-pollutants are shown in the Fig. 3. A comparison of micro-pollutant adsorbed activated carbon was also made to that of pure compound. The major peaks in the IR spectra of carbon and micro-pollutants are shown in Table 5.

The FTIR of the activated carbon (Fig. 3a) showed band at ~ 3400 cm^{-1} associated with –OH stretching vibration. The presence of prominent bands at 1658 and 1628 cm^{-1} with intensity subsequently decreasing after adsorption of the micro-pollutants were assigned to conjugated C = C stretching vibration. The bands observed at 1537 and 1363 cm^{-1} were assigned to (N-O) which might have formed as a result of steam activation of carbon. This suggests the presence of N and O containing groups on the carbon surface.

The spectrum of caffeine adsorbed activated carbon (Fig. 3b) showed bands at 1369, 1658 and 1726 cm^{-1} corresponding to C–N, C=N, C=O and C=C stretching vibrations, respectively. A weak band was also observed at 2955 and 3112 cm^{-1} arising due to CH_3 and aromatic C–H vibration.

The spectrum of ibuprofen (Fig. 3c) adsorbed activated carbon exhibited –OH and C=C bond stretching at 3404 and 1597 cm^{-1} respectively which was absent in the activated

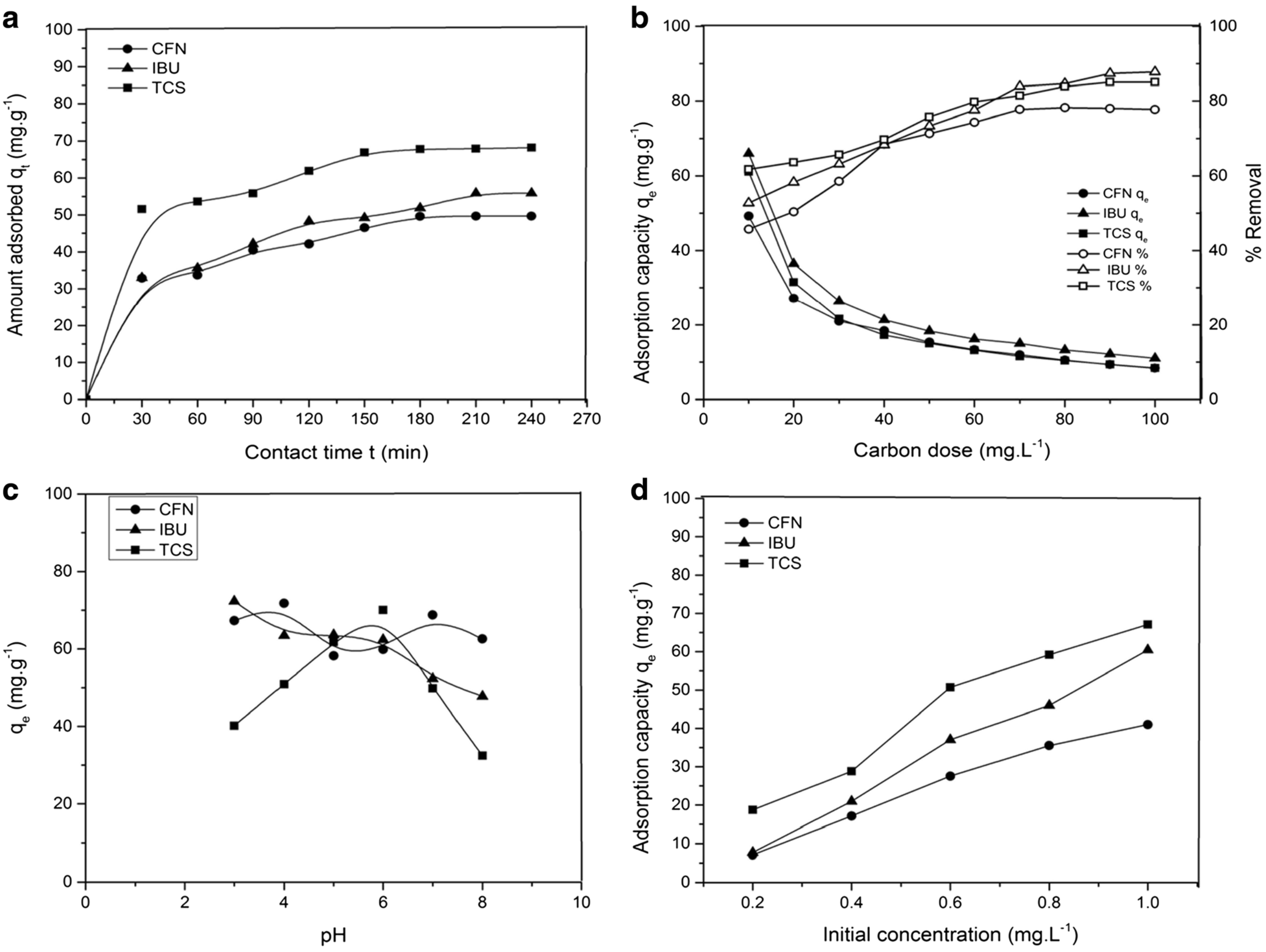


Fig. 4 Effect of experimental conditions: **a** contact time, **b** carbon dose, **c** solution pH and **(d)** initial concentration on PPCPs adsorption onto activated carbon

carbon spectrum. Other important peak observed at 1696 and 2364 cm^{-1} were assigned to acid carbonyl (C=O) and C–H stretching vibration.

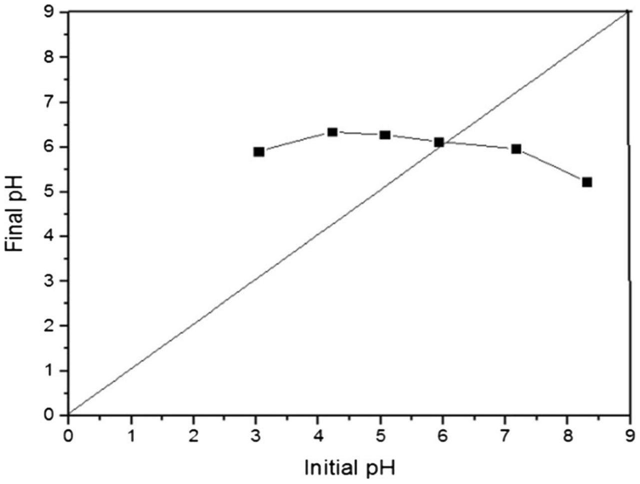


Fig. 5 Determination of pH$_{pzc}$ of Darco G 60 (adsorbent)

For triclosan (Fig. 3d), the strongest absorption bands arising from C–Cl stretching occurred in the low frequency range 911–673 cm^{-1}. The intensity of bands from C–O–C diaryl stretching vibration at 1179 and 1229 cm^{-1} was reduced in triclosan adsorbed activated carbon. Other important band of medium intensity was observed at 1367 cm^{-1} due to phenolic hydroxyl bending vibration.

Adsorption studies The effect of various experimental conditions viz. contact time, adsorbent dosage, pH and initial concentration were evaluated. No change in PPCPs concentration was found in control experiments, i.e. without the adsorbent.

Effect of contact time

Experiments were conducted at 30 °C using a minimum dose of 10 mg L^{-1} of activated carbon for adsorption of 1 mg L^{-1} of each micro-pollutant (Fig. 4a). The experimental initial concentration (C_0) was found to be 1.125 mg L^{-1} for caffeine, 1.252 mg L^{-1} for ibuprofen and 1.120 mg L^{-1} for triclosan. After a contact time of 4 h, caffeine concentration was found

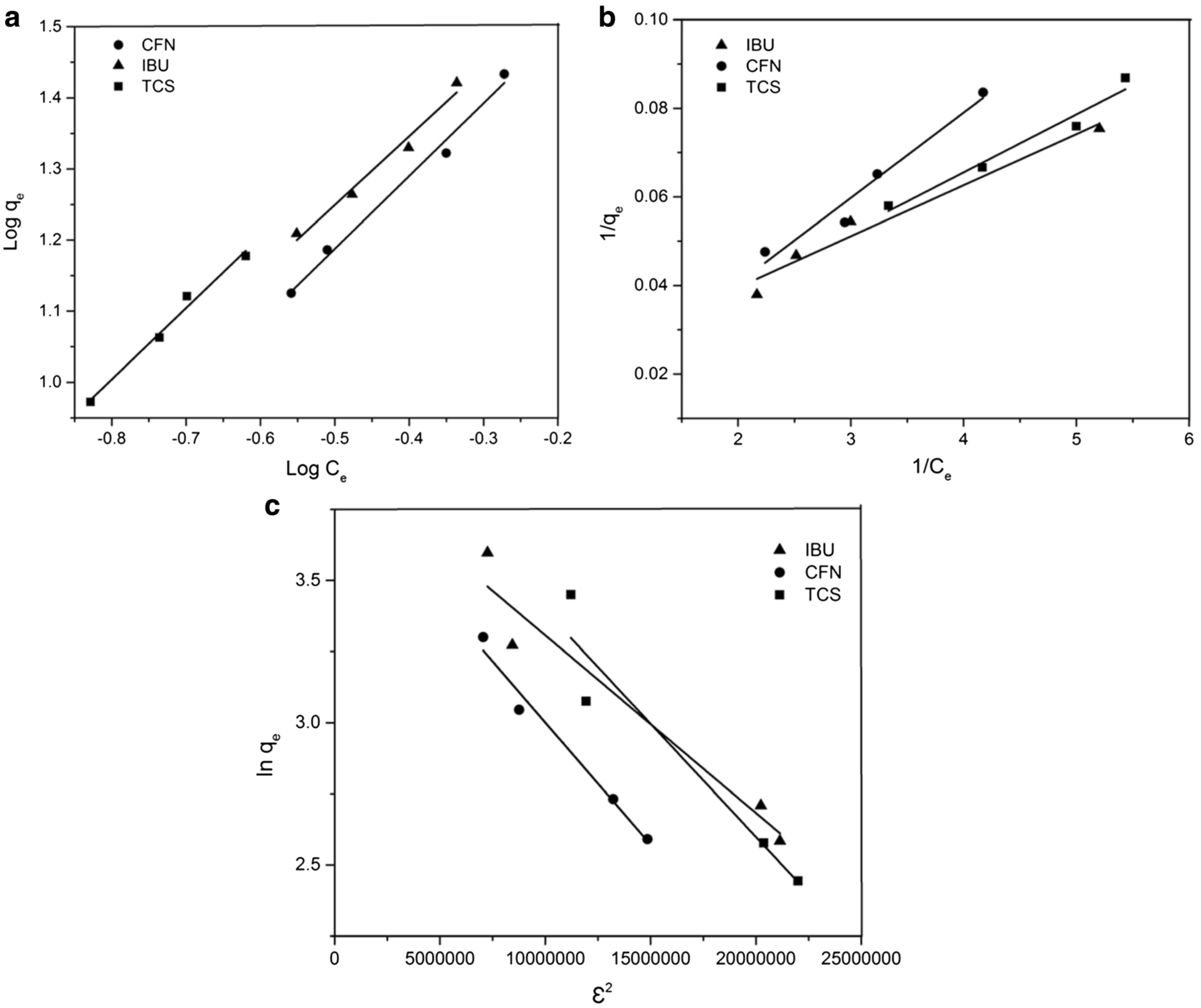


Fig. 6 **a** Freundlich, **b** Langmuir and **c** D-R isotherm model for PPCPs adsorption on activated carbon

to decrease from 1.125 to 0.628 mg L^{-1} (44.1% removal), ibuprofen from 1.253 to 0.593 mg L^{-1} (52.7% removal) and triclosan from 1.120 to 0.438 mg L^{-1} (60.8% removal).

It was found that the adsorption capacity increased with the increased in agitation time until equilibrium was achieved. From the graph of adsorption capacity against agitation time, it is clear that after the optimum time was reached, further agitation did not increase the adsorption capacity. Hence, the optimum contact time for caffeine and triclosan adsorption was 180 min while 210 min for ibuprofen.

Effect of dose

Maximum removal efficiency was determined by varying adsorbent dose from 10 to 100 mg L^{-1} at 10 doses (Fig. 4b), contact time of 4 h, temperature 30 °C, keeping a constant

Table 6 Freundlich, Langmuir and D-R parameters for PPCPs adsorption on activated carbon

Micro-pollutant	Freundlich parameters				Langmuir parameters				D-R parameters			
	R^2	$1/n$	K_f	q_m	R^2	q_m	K_L	R_L	R^2	q_m	β	E (KJ mol^{-1})
Caffeine	0.9899	1.0	48.7	52.3	0.9612	51.8	0.1	0.9	0.9800	47.4	9×10^{-8}	2.36
Ibuprofen	0.9775	0.9	54.0	67.1	0.9653	60.6	1.4	0.4	0.9499	50.8	6×10^{-8}	2.88
Triclosan	0.9786	1.0	72.0	71.5	0.9653	76.3	1.0	0.5	0.9221	65.9	8×10^{-8}	2.50

Table 7 Comparison of adsorption capacities of activated carbons for removal of caffeine, ibuprofen and triclosan

Adsorbent	Caffeine q_m (mg g^{-1})	Ibuprofen q_m (mg g^{-1})	Triclosan q_m (mg g^{-1})	Matrix	Reference
Darco G60 PAC	52.3	67.1	71.5	Ultrapure water	This study
Commercial PAC (Panreac)	12.6	–	–	WWTP effluent	Acero et al. 2012
Water hyacinth-derived biochar	2.48	–	–	Ultrapure water	Ngeno et al. 2016
Pulp mill sludge-derived charcoal	–	12.9 12.6	–	Ultrapure water STP secondary effluent	Coimbra et al. 2015
F400	–	62.2	–	Ultrapure water	Delgado et al. 2015
Charcoal-based GAC	–	–	18.5–70.4 (at various pH)	Ultrapure water	Behera et al. 2010
Biosolid-derived biochar	–	–	0.518	Ultrapure water	Tong et al. 2016
			0.239	WWTP secondary effluent	

solution volume of 100 cm^3 and adsorbate concentration of 1 mg L^{-1}. The experimental initial concentration (C_0) was found to be 1.076 mg L^{-1} for caffeine, 1.253 mg L^{-1} for ibuprofen and 0.993 mg L^{-1} for triclosan. At a carbon dose of 100 mg L^{-1}, ~ 78% caffeine removal, ~ 88% ibuprofen removal and ~ 85% triclosan removal was achieved.

It should be highlighted that at dosage < 60 mg L^{-1}, the removal followed the order CFN < IBU < TCS, i.e. in accordance to log K_{ow}. This behaviour was more pronounced at even lower adsorbent dosage, i.e. between 10 and 30 mg L^{-1}. Beyond 60 mg L^{-1} adsorbent, ibuprofen was slightly more adsorbed than triclosan. Finally, at higher dosage, the removal was almost equal for the hydrophobic micro-pollutants irrespective of their log K_{ow} owing to overcrowding of adsorbent particles thus overlapping the adsorption sites (Khalid et al. 2015). The adsorption capacity (q_e) decreased with increase in adsorbent dosage. The q_m was found to be slightly higher for ibuprofen than triclosan which could be attributed to the difference in their initial concentrations. Thus, implying the dependence of q_m on the micro-pollutant initial concentration. It was found that caffeine percentage removal had increased from 45.6 to 77.7% on increasing adsorbent dosage up to 80 mg L^{-1}. Further increase in the adsorbent dosage led to decrease in amount of caffeine adsorbed. Similarly, ibuprofen removal efficiency increased from 52.6 to 87.8% and that of triclosan from 61.7 to 85% on increasing dose from 10 to 100 mg L^{-1}. The adsorption capacity of the carbon decreased from 49.2 to 8.4 mg g^{-1} for caffeine, 65.9 to 10.9 mg g for ibuprofen and 61.3 to 8.4 mg g for triclosan.

Effect of pH

The pH_{pzc} is an important property used to determine net surface charges of the activated carbon in aqueous medium. At pH_{pzc}, surface functional groups have no contribution towards pH of the solution. It has been reported by Couto et al. (2015) that pH_{pzc} has significance in adsorption of micro-pollutants like caffeine on activated carbon in aqueous medium. To determine pH_{pzc} (point of zero charge), initial pH versus final pH was plotted and pH_{pzc} was taken as the point where $pH_{initial} = pH_{final}$. The pH_{pzc} calculated by this method was 6.2 for the activated carbon (Fig. 5).

The pH dependent study was carried out at 30 °C using 1 mg L^{-1} as initial concentration of targeted PPCPs. The pH was varied from 3 to 8 using a carbon dose of 10 mg L^{-1}.

Caffeine removal efficiency at pH = pH_{pzc} was found to be ~ 50%. As shown in Fig. 4c, caffeine adsorption was not much affected by pH except at lower pH of 3 and 4 where removal efficiency was slightly enhanced to ~ 56%. This is because at pH 3 and 4, activated carbon is positively charged (pH < pH_{pzc}) while caffeine with a heterocyclic-N group is mostly in its neutral form. Hence, enhanced adsorption at lower pH could be attributed to non-electrostatic interactions. The maximum caffeine adsorption capacity (~ 71.7 mg g^{-1}) by the adsorbent was obtained at pH 4.

The amount of ibuprofen adsorbed by the activated carbon decreased with increase in pH. In terms of removal efficiency, it was found to be > 50% between pH 3–6 which reduced to ~ 45% at pH > 6. This could be attributed to the increased deprotonation of ibuprofen having a carboxylic acid group (−COOH). At high pH, (pH > pH_{pzc}), the activated carbon surface is negatively charged causing repulsive interactions between ibuprofen and activated carbon (Essandoh et al. 2015). At pH = pH_{pzc}, 59% ibuprofen removal was obtained. The maximum adsorption capacity (~ 72.3 mg g^{-1}) by the adsorbent was obtained at pH 3.

The maximum triclosan adsorption capacity (~ 70 mg g^{-1}) of the adsorbent was obtained at pH 6.0 (pH = pH_{pzc}). Triclosan removal efficiency was > 50% between pH 3–6 and < 50% at pH > 6. This is because increase in pH causes partial or full de-protonation of surface functional groups thus creating net negative charge on triclosan. Thus, reducing sorption capacity owing to electrostatic repulsion between the deprotonated triclosan and minus charged surface of the carbon

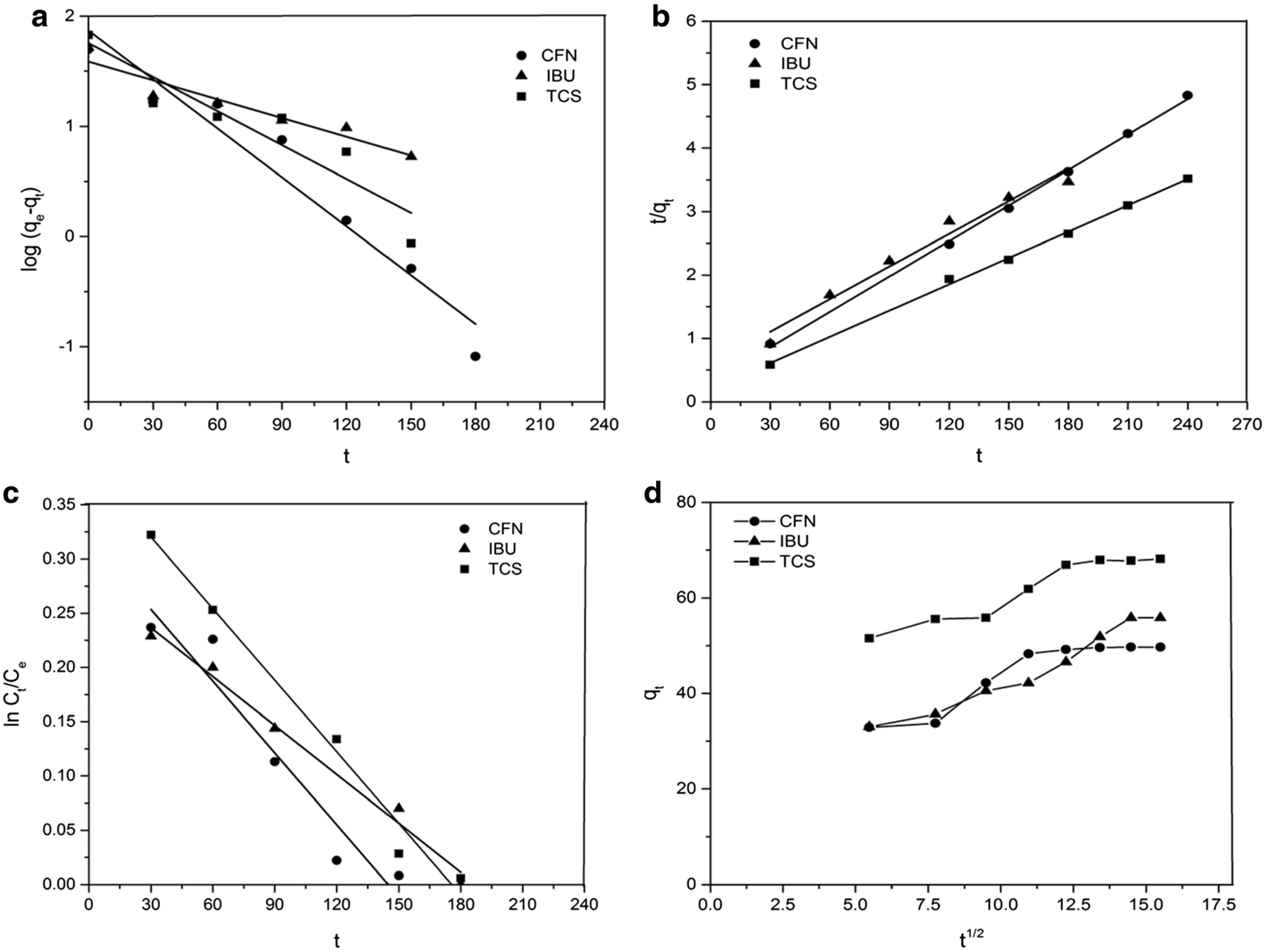


Fig. 7 Kinetics models: **a** pseudo-first order, **b** pseudo-second order, **c** particle diffusion and **d** intra-particle pore diffusion model for PPCPs adsorption on activated carbon

(Behera et al. 2010). At pH 6 (pH = pH_{pzc}), there are no surface charges on the activated carbon and hence, it can form H-bond with phenoxy hydroxyl of triclosan. This is the region where maximum triclosan adsorption occurs (75% removal).

Effect of initial concentration

The effect of initial concentration of micro-pollutant was studied by varying micro-pollutant concentration from 200 to 1000 μg L^{-1}, at 30 °C, contact time 4 h and adsorbent dose 10 mg L^{-1}. Figure 4d shows the trend in variation in adsorption capacity with initial concentration. The adsorption capacity increased with increasing initial concentrations. It was also observed that at C_0 = 200 μg L^{-1}, the adsorption capacity of carbon for caffeine and ibuprofen was not much different. However, triclosan adsorption capacity was always higher than other micro-pollutant even at low initial concentrations. Thus, hydrophobic effect was observed even at lower concentration for triclosan.

Table 8 Pseudo-first order and pseudo-second order parameters for PPCPs adsorption on activated carbon

Micro-pollutant	Pseudo-first order model				Pseudo-second order model			
	R^2	$q_{e\ exp.}$ (mg g^{-1})	$q_{e\ calc}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$q_{e\ exp.}$ (mg g^{-1})	$q_{e\ calc}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})
Caffeine	0.9442	49.6	74.3	0.034	0.9970	49.6	51.3	0.0026
Ibuprofen	0.9346	51.8	46.6	0.016	0.9669	51.8	51.8	0.0012
Triclosan	0.8956	67.8	72.8	0.031	0.9972	67.8	69.4	0.0022

Table 9 Particle and intra-particle diffusion parameters for PPCPs adsorption on activated carbon

Contaminant	Particle diffusion model		Intra-particle pore diffusion model		
	R^2	K_p (mg g^{-1} min^{-1})	R^2	K_t (mg g^{-1} min$^{-0.5}$)	c
Caffeine	0.9300	0.0022	0.8530	1.9544	22.58
Ibuprofen	0.9873	0.0015	0.9824	0.1110	29.69
Triclosan	0.9848	0.0022	0.9842	0.0869	50.25

Adsorption isotherm

The sorption isotherms of caffeine, ibuprofen and triclosan were studied by fitting the data to Freundlich, Langmuir and D-R (Dubinin - Radushkevish) isotherm models (Fig. 6).

In the Freundlich model, 1/n was found to be between 0 and 1 for all the three micro-pollutants under study which indicates favourable adsorption (Table 6). The correlation coefficient (R^2) for all three micro-pollutants was found to be higher for the Freundlich model than Langmuir model. The Freundlich maximum adsorption capacity was found to be positively correlated with the log K_{ow} of the micro-pollutants.

The results were compared to previous literature reported on activated carbons (Table 7). The adsorption capacity for Darco G 60 was considerably higher than that reported earlier especially for triclosan. It is noteworthy that a detailed study on this activated carbon using the targeted PPCPs has not been conducted so far. Also, there exists very scarce literature on the same.

To deduce apparent energy of adsorption (E), data was fitted to the D-R isotherm model (calculated using formulae mentioned in Table 3). The values of E were found to be < 8KJ/mol for targeted compounds. Thus, indicating that adsorption is mainly dominated by physisorption as reported earlier (Guedidi et al. 2014) for ibuprofen.

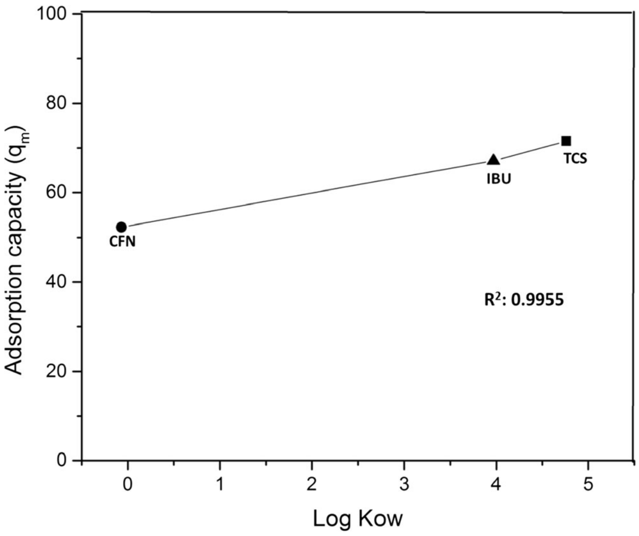


Fig. 8 Linear fit of log K_{ow} value and adsorption capacity of micro-pollutants on Darco G 60

Adsorption kinetics

The reaction kinetics was determined by PFO and PSO models (Fig. 7a, b) using equations mentioned in Table 2. The correlation coefficient (R^2) for the PSO model was higher than that of PFO model (Table 8). Also, there was a good agreement between the experimental sorption capacity ($q_{e\ exp}$) and that calculated ($q_{e\ calc}$) using PSO model for the three micro-pollutants under study. Thus, PPCPs adsorption on activated carbon followed pseudo-second order kinetics.

The reaction kinetics of adsorption was also studied using diffusion-based models: particle and intra-particle diffusion models. The linear plots of both diffusion models are shown in the Fig. 7c, d and values of various parameters mentioned in Table 9. It was found that the R^2 value of particle diffusion model was higher thus indicating particle diffusion as the rate-limiting step.

On plotting q_t versus $t^{1/2}$ for intra-particle diffusion model, a multi-linear graph not passing through origin was observed for the three contaminants. A multi-linear plot indicates influence of two or more steps on the adsorption process. Thus, implying that rate is determined not solely by intra-particle pore diffusion for PPCPs adsorption on activated carbon (Yakout and Elsherif 2010).

Mechanism of micro-pollutant adsorption on Darco G 60

As per literature reported, caffeine adsorption on carbonaceous materials mostly occurs by hydrophobic interactions (Álvarez-Torrellas et al. 2016). From the pore distribution studies, the average pore diameter of the activated carbon was found to be 3.07 nm. The molecular size of caffeine is 0.98 × 0.87 × 0.56 nm. Similarly, ibuprofen has molecular dimensions of 1.06 × 0.57 × 0.46 nm while that of triclosan is 1.42 × 0.69 × 0.75 nm. The results indicated that better adsorption was achieved for adsorbate with molecular size closer to the pore diameter of adsorbent; also referred to as pore-filling mechanism (Newcombe et al. 1997).

To account for hydrophobicity effects of micro-pollutant on adsorption process, log K_{ow} was plotted against their adsorption capacity (q_m). As evident from Fig. 8, it was observed that there existed a linear relationship between q_m and log K_{ow} with a high correlation coefficient (0.9955). The FTIR spectra of micro-pollutants also exhibited significant decrease in intensity of conjugated C=C band as compared to the activated carbon, thus implying the existence of hydrophobic and pi-pi interaction between the micro-pollutants and carbon surface. It is noteworthy that hydrophobic interactions might not be directly responsible for micro-pollutant adsorption onto the activated carbon, but its impact on the adsorption behaviour could not be neglected (Zhao et al. 2016).

Conclusions

This study investigated the sorption characteristics of three of the most frequently occurring micro-pollutants in water and wastewater. The effect of several experimental conditions such as contact time, activated carbon dose, pH and initial concentration was evaluated for each of the three micro-pollutants using batch adsorption studies. The adsorbent was characterised and experimental data was fitted into various isotherms and kinetic models to deduce mechanism of adsorption. The results are reported as under:

(1) The adsorption capacity and removal efficiency were found in the order of the octanol-water partition coefficient (log K_{ow}) of the micro-pollutants.
(2) With a dosage of 100 mg L^{-1}, maximum removal was achieved. The adsorbent was found to more effectively adsorb hydrophobic micro-pollutants at low dosage. Thus, proving a potential adsorbent for efficient micro-pollutant removal.
(3) The adsorptive removal was not much affected by pH for hydrophilic micro-pollutant; caffeine. Ibuprofen adsorption was significantly affected by pH with better removal efficiency at acidic pH. Triclosan showed maximum adsorption at $pH = pH_{pzc} = 6$.
(4) Darco G 60 showed better adsorption for triclosan even at lower initial concentrations.
(5) The FTIR spectra showed C=C and C=O functional groups as major adsorption sites for micro-pollutant solutions.
(6) The pore size distribution study revealed that pore diameter of the adsorbent was in good agreement with the molecular size of the PPCPs.
(7) Sorption coefficients were well fitted to the Freundlich adsorption isotherm model for all micro-pollutants.
(8) The adsorption process followed the PSO model indicating both adsorbent as well as adsorbate concentrations as potential contributors towards determination of the rate of reaction.
(9) The adsorption process was found to be physisorption with adsorption occurring through particle-diffusion.

The results obtained in the present study systematically correlate the effect of hydrophobicity/lipophilicity on sorption properties of the carbon. The study established that this activated carbon is as effective as other adsorbents in removing highly hydrophobic contaminants which are of more concern considering their bioaccumulation potential. The results also established that the activated carbon may be functionalized to further enhance adsorption of more hydrophobic micro-pollutants from water.

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