



Multiparametric investigation of competitive and noncompetitive sorption characteristics of SMP fractions (carbohydrate and protein) on activated carbon

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ABSTRACT

Sorption characteristics of soluble microbial products (SMPs) as carbohydrate and protein on activated carbon were investigated. Batch experiments were conducted to evaluate the sorption kinetics and the equilibrium conditions. The parameters studied included initial SMP concentration (50–200 mg/L), activated carbon dosage (0.25–50 g/L), contact time (0.02–4 h), particle size of activated carbon used (5–75 μm , 75–850 μm , and 850–1000 μm), and presence of one or both SMP fractions. The equilibrium sorption of carbohydrate and protein were significantly affected by the presence of the second SMP fraction in the solutions. Adsorption isotherms were expressed by the Langmuir and Freundlich models. The adsorption rates under noncompetitive and competitive conditions were analyzed with kinetics-based Lagergren pseudo-first order and pseudo-second order models; and diffusion-based external diffusion and Weber–Morris intraparticle models. Both SMP fractions were removed effectively, however, sorption of protein was significantly better than that of carbohydrate in all cases. The relatively significant effect of particle size on sorption of protein indicates that protein is most likely adsorbed as a single layer on the carbon surface. For the carbohydrate, the increase in particle size did not decrease the sorption significantly indicating that carbohydrate may be adsorbed in multiple layers or may diffuse into the porous matrix more effectively.

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1. Introduction

Effluents from biological wastewater treatment processes contain a variety of soluble organic compounds, including residual substrates, intermediate and end products from biotransformation reactions as well as soluble microbial byproducts (SMPs). The term SMP has been defined to represent the pool of organic compounds that are released into the solution from substrate metabolism (usually with biomass growth) and biomass decay [1]. SMP constitutes the majority of the soluble organic matter in effluents from biological treatment processes [2–6]. Therefore, the presence of SMP in the effluents from biological treatment processes indicates that there are lower limits of SMP which are achievable depending on the process conditions [1]. For some biological processes, SMP could be more toxic than the original organic compounds in the wastewater. Rappaport et al. [7] reported more significant mutagenic response with the secondary effluents than those with primary effluents. Some SMP are inhibitory to nitrification process [8]. In addition, SMP in the biological effluents can affect the performance of downstream treatment processes. For example, SMP may

affect the biofilm structure, viscosity, hydrophobicity, flocculation characteristics and other physical properties of the sludge [9–12].

Activated carbon adsorption process has been widely used in removing soluble organics as well as SMP from wastewater. Carbon has a strong surface affinity for organic compounds especially carbohydrate and protein even when present at low concentrations [13,14]. Carbon adsorption processes are generally considered for applications where a high quality of water is desired (e.g., for reuse of the wastewater effluent) [15]. Activated carbon has a porous structure with high specific surface (area/unit weight); however, the utilization of surface depends on the activation characteristics, roughness, and accessibility of the interior surfaces [16]. Fig. 1 illustrates the diffusive and non-diffusive sorption mechanisms of SMP on activated carbon surface. The compounds with smaller molecular size can diffuse into the porous structure of carbon particles; hence, exhibit a multi layered sorption profile. On the other hand, larger molecules have limited ability to diffuse into the porous matrix; hence, can be adsorbed primarily on the exterior surfaces. For solutions containing multiple compounds with affinity for carbon surfaces, the utilization of carbon surface may favor some compounds due to their ability to interact with the carbon surface in multiple configurations and mechanisms as well as size and flexibility of the molecules competing for the available sites on the surface. Treatability of SMP with advanced treatment

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Nomenclature

A	total interfacial area of the particles (cm^2)
b	equilibrium constant in Langmuir model (L/g)
C_0	initial SMP concentration (mg/L)
C_e	equilibrium SMP concentration (mg/L)
C_t	SMP concentration in solution at time t (mg/L)
d	mean particle diameter of activated carbon (cm)
k_1	pseudo-first order rate constant (L/min)
k_2	pseudo-second order rate constant (g/mg min)
k_{id}	intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$)
k_f	initial external mass transfer coefficient
k_F	Freundlich constant (mg/g)
m	adsorbent dosage (g/cm^3)
m_s	weight of activated carbon (g)
n	Freundlich constant
q_e	sorption capacity at equilibrium (mg/g)
$q_{e,\text{cal}}$	calculated sorption capacity (mg/g)
$q_{e,\text{exp}}$	experimental sorption capacity (mg/g)
q_t	sorption capacity of activated carbon at time t (mg/g)
Q_0	Langmuir constant related to monolayer capacity (mg/g)
r^2	correlation coefficient
R	percent of removed metal from aqueous solution (%)
t	time (min)
V	volume of solution (L)
ρ	apparent density of adsorbent (g/cm^3)

techniques (i.e., oxidation, ozonation, synthetic resin adsorption, coagulation and breakpoint chlorination) have been studied by several researchers [17–20]. Among the treatment processes investigated, activated carbon adsorption has been identified as one of the most effective methods for removing SMP [21–24].

The sorption models developed for single component cases may not be adequate when there is more than one component in the solution at relatively high concentrations. Due to interactions of the components with each other as well as the sorbent, the sorption process is affected both from sorption kinetics and sorption equilibrium perspectives. Under the competitive conditions, the time

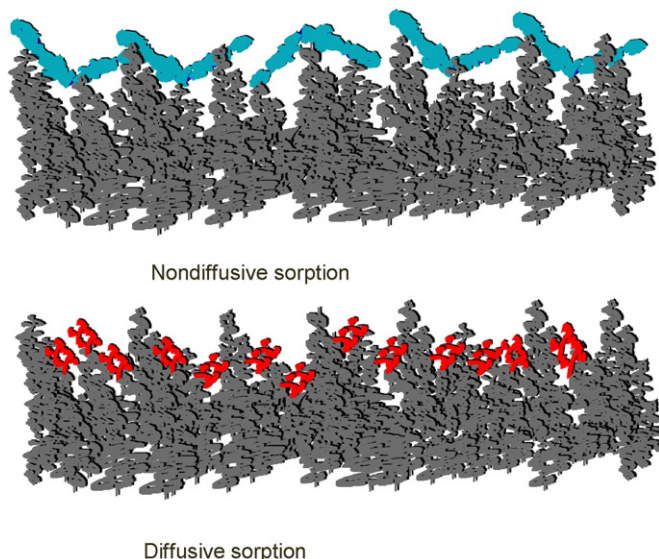


Fig. 1. Schematic representation of SMP adsorption mechanism on activated carbon.

to reach equilibrium may become longer as the different components compete for surface availability by near surface interactions and dynamics of molecular configuration at the surface to minimize surface energy. The difference in sorption rates could also significantly reduce the sorption of the components. The component with slower sorption kinetics would have more significant reduction in sorption efficiency at equilibrium. Objectives of this study were to investigate the adsorption characteristics of soluble microbial products as carbohydrate and protein on activated carbon and evaluate the adequacy of adsorption models for different SMP fractions under competitive and noncompetitive sorption conditions. The study was conducted in four phases: (1) development of individual adsorption profiles of SMP fractions present in synthetic wastewater on activated carbon under equilibrium conditions, (2) investigation of competitive adsorption characteristics when more than one SMP fraction is present in different proportions, (3) evaluation of sorption kinetics and mechanism, and (4) modeling of adsorption process. Batch sorption experiments were conducted with synthetic wastewater which contained either one or both SMP fractions (carbohydrate or protein) at different proportions. The parameters studied included initial SMP concentration (50–200 mg/L), activated carbon dosage (0.25–50 g/L), contact time (0.02–4 h), particle size of activated carbon (5–75 μm , 75–850 μm , and 850–1000 μm), and presence of one or two SMP fractions (i.e., carbohydrate and protein). Adsorption isotherms were developed for noncompetitive and competitive conditions and expressed by the Langmuir and Freundlich models. The experimental data were analyzed with both reaction based and diffusion based kinetic models. Sorption mechanisms for SMP were analyzed for carbohydrate and protein fractions based on the adequacy of the models.

2. Experimental

2.1. Materials

2.1.1. Activated carbon specifications

The batch sorption studies were conducted using coal based activated carbon (Calgon, Activated Carbon Technologies, USA) with a specific surface of $>1000 \text{ BET m}^2/\text{g}$ and iodine number of $>800 \text{ mg/g min}$. Coal based activated carbon has high number of micropores (diameter range less than 2 nm) and relatively fewer macropores (diameter range above 25 nm) as specified by the manufacturer. The pore volume distributions for micropores are about 0.23 mL/g carbon for micropores, 0.18 mL/g carbon for mesopores, and 0.21 mL/g carbon for macropores. The activated carbon (AC) had a maximum ash content of 15% and maximum moisture content of 4%. Prior to use, the AC was rinsed with distilled water to remove the fines and oven dried at 105°C .

2.1.2. Model wastewaters

Many researchers have recognized that the soluble organic matter in effluents from biological treatment processes primarily consist of SMP. To better define the system conditions, many researchers have used synthetic solutions to model wastewaters. These solutions are sometimes very simple with one easily biodegradable substrate (i.e., glucose). The compositions of the model wastewaters presented in Table 1 were selected based on the previous studies using synthetic wastewater (i.e., glucose and BSA) [21]. The glucose and protein concentrations were used higher than the expected levels at biological treatment process effluent in order to easily observe the interactions between the two SMP fractions. At lower levels, the competitive interactions may not be significant.

Five different model wastewaters were prepared to represent the aerobic MBRs treating synthetic wastewater compositions with

Table 1
Compositions of synthetic wastewater (Models 1–5 wastewaters).

Constituent	Concentration (mg/L)				
	Model 1	Model 2	Model 3	Model 4	Model 5
Glucose	100	–	150	100	50
BSA	–	100	50	100	150
KH ₂ PO ₄	8.5	8.5	8.5	8.5	8.5
(NH ₄) ₂ SO ₄	7.5	7.5	7.5	7.5	7.5
NaHCO ₃	40	40	40	40	40
MgSO ₄ ·7H ₂ O	7.5	7.5	7.5	7.5	7.5
CaCl ₂ ·2H ₂ O	1.5	1.5	1.5	1.5	1.5
KCl	1.5	1.5	1.5	1.5	1.5
NaCl	7.5	7.5	7.5	7.5	7.5
CuSO ₄ ·5H ₂ O	0.015	0.015	0.015	0.015	0.015
MnCl ₂ ·4H ₂ O	1.0	1.0	1.0	1.0	1.0
ZnSO ₄ ·7H ₂ O	0.038	0.038	0.038	0.038	0.038
FeCl ₃ ·6H ₂ O	2.5	2.5	2.5	2.5	2.5

different carbohydrate and protein concentrations. Table 1 presents the compositions of the model wastewaters used in the study. The solutions containing single SMP fraction as carbohydrate (glucose in model 1 wastewater), single SMP fraction as protein (bovine serum albumin in model 2 wastewater), and both SMP fractions (protein and carbohydrate) (model 3–5 wastewaters) were prepared by diluting stock solutions of carbohydrate and protein to the desired concentrations. Stock solutions of carbohydrate and protein were prepared by dissolving the exact quantities of glucose (Merck) and bovine serum albumin (BSA) with of 99.5% purity (Merck and Co., Inc., Whitehouse Station, NJ, USA), in 1 L of double-distilled water, respectively. The ranges of concentrations of both components prepared from stock solutions varied between 25 and 800 mg/L. The test solutions containing desired concentrations of carbohydrate and protein were prepared by diluting 1.0 g/L of stock solutions of carbohydrate and protein and mixing them in desired proportions. Before adding the activated carbon, the pH of each test solution was adjusted to 7.2 ± 0.2 with 0.01 N H₂SO₄ or NaOH solutions.

2.2. Methods

2.2.1. Batch experiments

The equilibrium conditions and sorption kinetics were analyzed by batch experiments which were performed in 125 mL Erlenmeyer flasks. Specific amounts of activated carbon were added into 50 mL wastewater sample containing known concentrations of SMP fractions as carbohydrate, protein or both. The Erlenmeyer flasks were placed on the orbital shaker at 175 rpm for 1 day at room temperature ($23 \pm 2^\circ\text{C}$) to ensure equilibrium conditions were reached. The solid phase (activated carbon) was separated by filtration through a 0.45 μm pore cellulose acetate filter. The filtrate was analyzed with spectrophotometer to determine the final SMP (carbohydrate and protein) concentration. Each test was conducted in duplicates and mean values were used in the analysis of data. Standard deviation and analytical errors were calculated and maximum errors were found to be within $\pm 3\%$ of the measured values.

The effects of agitation time, initial SMP concentration, adsorbent dosage and particle on the sorption characteristics of SMP were investigated. To study the effect of particle size, the activated carbon was sieved through standard sieves (ASTM D422) to better control the particle size. By sieving, the activated carbon was classified into three particle size ranges as 5–75 μm , 75–850 μm , and 850–1000 μm . Batch sorption experiments were conducted with carbon particles in each size range while keeping the other test conditions constant (i.e., SMP concentration: 100 mg/L, pH: 7.2 ± 0.2 , amount of adsorbent: 25 g/L, contact time: 1 day, agitation speed: 175 rpm, and temperature: $23 \pm 2^\circ\text{C}$).

The effect of the activated carbon dosage was studied by varying the amount of carbon (0.25–50 g/L) while keeping the other test parameters constant (i.e., SMP concentration: 100 mg/L, pH: 7.2 ± 0.2 , contact time: 1 day, agitation speed: 175 rpm, and temperature: $23 \pm 2^\circ\text{C}$). The effect of the initial SMP concentration was investigated (50–200 mg/L SMP) at pH 7.2 ± 0.2 . Samples of synthetic wastewater containing different concentrations of SMP (carbohydrate, protein, or both) were added into the Erlenmeyer flasks with 25 g/L of activated carbon at room temperature ($23 \pm 2^\circ\text{C}$) and placed on the orbital shaker at 175 rpm for 24 h to develop the adsorption equilibrium profile.

2.2.2. SMP analysis

The protein analyses were performed according to method described by Lowry et al. [25]. BSA was used as the standard and the results were expressed in mg equivalent of BSA per gram of adsorbent. Carbohydrate was determined by the phenol-sulfuric acid method developed by Dubois et al. [26]. Glucose was used as the standard and the results were expressed in mg equivalent of glucose per gram of adsorbent. All samples were analyzed with UV–vis spectrophotometer (Turner Spectrophotometer SP 830) at the wavelength of 490 nm for carbohydrate or at 660 nm for protein. Calibration curves were prepared for the concentration range between 1 and 200 mg/L. Precision of the parallel measurements was $\pm 3\%$ SD. The pH measurements were conducted with a glass electrode (WTW 440i Model pH meter).

3. Data analysis and modeling

3.1. Data analysis

The SMP adsorption capacity of the activated carbon was estimated by mass balance:

$$q_t = \frac{(C_0 - C_t)V}{m_s} \quad (1)$$

where q_t is the adsorbed SMP amount (mg/g), V is the volume (L) of solution, C_0 is the initial SMP concentration in wastewater (mg/L), C_t is the equilibrium SMP concentration (mg/L), m_s is the amount of adsorbent (g).

The SMP removal efficiency was calculated by Eq. (2):

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

where C_0 is the initial SMP concentration (mg/L), C_t is the SMP concentration at time t (mg/L), R is the SMP removal efficiency (%).

3.2. Kinetic models

Adsorption kinetics describes the rate of sorption which controls the residence time of adsorbate at the solid–liquid interface. The SMP sorption kinetics was analyzed with both reaction-based and diffusion-based models as summarized in Table 2. The models used included the Lagergren pseudo-first order [27] and pseudo-second order [28] for reaction-based kinetics (Eqs. (3) and (4)); external [29] and Weber–Morris intraparticle [30] for diffusion-based kinetics (Eqs. (5) and (6)).

3.3. Equilibrium isotherms

The equilibrium state of a compound in the solid and aqueous phases can be represented by adsorption isotherms when the adsorption process reaches the equilibrium at constant temperature. The adsorption isotherm is developed based on the assumptions that every adsorption site has the same affinity and that the ability of a particle to bind is independent of whether or not

Table 2
Empirical models used for data analyses.

	Non-linear form	Linear form	Eq. No.
<i>Reaction-based kinetic models</i>			
Lagergren pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}(t)$	(3)
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t)$	(4)
<i>Diffusion-based kinetic models</i>			
External diffusion	$\frac{C_t}{C_o} = e^{-k_f(A/V)t}$	$\ln \frac{C_t}{C_o} = -k_f \frac{A}{V}(t)$ and $\left[\frac{A}{V} = 3 \frac{m}{\rho d}\right]$	(5)
Weber–Morris intraparticle diffusion	$q_t = k_{id}(t)^{1/2}$	$\log q_t = \log(k_{id}) + \frac{1}{2} \log(t)$	(6)
<i>Equilibrium isotherm models</i>			
Langmuir	$q_e = \frac{Q_o b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o}$	(7)
Freundlich	$q_e = k_F C_e^{1/n}$	$\log q_e = \log k_F + \frac{1}{n} \log C_e$	(8)

adjacent sites are occupied [31,32]. The most widely used isotherm models are the Langmuir and Freundlich models [31,33]. The Langmuir isotherm applies to adsorption on homogenous surfaces with negligible interaction between adsorbed molecules. However, the Freundlich isotherm describes equilibrium on heterogeneous surfaces and hence does not assume monolayer capacity [31,33]. The adequacy of the Langmuir and Freundlich isotherms were compared using the linear forms of the Langmuir and Freundlich equations as presented in Table 2 (Eqs. (7) and (8)).

4. Results and discussion

The combined effects of two or more components present in solution on the sorption process depend on both the physico-chemical parameters of the solution (i.e., pH, temperature, initial solute concentration), number of solutes competing for binding sites, solute–solute interactions, solute concentrations, order of solute addition and residence time [34]. In this study, simultaneous adsorption characteristics of carbohydrate and protein on activated carbon were studied under noncompetitive and competitive conditions with batch experiments.

4.1. Effect of particle size of carbon

The effect of particle size of carbon (5–75 μm , 75–850 μm , and 850–1000 μm) on individual and competitive adsorption of SMP fractions is presented in Table 3. When the particle size was increased from 5–75 μm to 850–1000 μm , the individual adsorption capacity decreased for both carbohydrate and protein. Particle size of the activated carbon did not have a significant effect on the removal efficiency of carbohydrate when there was no protein

in the solution and when carbohydrate concentration was significantly higher than that of protein (i.e., for Model 1 wastewater: 63.12% for 5–75 μm and 59.82% for 850–1000 μm). However, the effect of carbon particle size had a significant effect on protein removal efficiency in all cases studied (i.e., for Model 2 wastewater: 96.00% for 5–75 μm and 34.28% for 850–1000 μm). The fact that protein sorption decreased more significantly with increase in particle size indicates that protein may be sorbed only on the exterior surfaces of carbon or as monolayer. For carbohydrate, the increase in particle size did not decrease the adsorbed SMP amount significantly which indicates that carbohydrate was not affected by the change in the available surface area.

Increasing the particle size from 5–75 μm to 850–1000 μm under the competitive adsorption conditions (i.e., both SMP fractions were present) resulted in a decrease for both carbohydrate and protein when the carbohydrate/protein ratio was 3/1 (model 3), 1/1 (model 4), and 1/3 (model 5). The results show that protein exhibits higher sensitivity to increasing surface area and has relatively stronger binding affinity to the activated carbon than carbohydrate under both individual and competitive sorption conditions. The relatively higher adsorption capacity at smaller particle size may be attributed to the fact that smaller particles possess larger surface areas.

4.2. Effect of carbon dosage

The amount of adsorbent is one of the critical parameters in design of activated carbon systems. Batch sorption studies conducted at different carbon dosages can help determine the optimum dosage [15]. In this study, SMP adsorption from synthetic wastewater onto activated carbon was studied by varying

Table 3

Effect of adsorbent particle size (5–75 μm , 75–850 μm , and 850–1000 μm) on SMP removal by activated carbon from synthetic wastewater (m_s : 25 g/L, pH: 7.2 \pm 0.2, T: 23 \pm 0.2 $^\circ\text{C}$, contact time: 24 h at 175 rpm).

Wastewater solution	Particle size (μm)	Carbohydrate		Protein	
		q_e (mg/g)	Removal efficiency (%)	q_e (mg/g)	Removal efficiency (%)
Model 1 (C only)	5–75	2.53	63.12	–	–
	75–850	2.45	61.19	–	–
	850–1000	2.39	59.82	–	–
Model 2 (P only)	5–75	–	–	4.29	96.00
	75–850	–	–	1.56	34.86
	850–1000	–	–	1.53	34.28
Model 3 (C/P=3/1)	5–75	3.96	68.64	2.80	95.64
	75–850	3.55	61.63	1.67	56.98
	850–1000	3.45	59.89	1.39	47.67
Model 4 (C/P=1/1)	5–75	3.76	76.18	4.38	95.90
	75–850	3.74	75.63	1.34	29.24
	850–1000	3.69	74.71	0.63	13.78
Model 5 (C/P=1/3)	5–75	1.99	96.92	5.91	93.66
	75–850	1.62	78.95	1.48	23.48
	850–1000	1.57	76.73	1.00	15.92

Table 4
Effect of adsorbent dosage on SMP removal by activated carbon from synthetic wastewater (pH: 7.2 ± 0.2 ; T: $23 \pm 2^\circ\text{C}$; particle size: 5–75 μm , contact time: 24 h at 175 rpm).

Wastewater	Carbon dose (g/L)	Carbohydrate		Protein	
		q_e (mg/g)	Removal efficiency (%)	q_e (mg/g)	Removal efficiency (%)
Model 1 (C only)	0.25	16.36	4.09	–	–
	0.5	15.91	7.95	–	–
	1	14.54	14.53	–	–
	2.5	7.59	18.96	–	–
	5	6.20	30.99	–	–
	10	4.35	43.48	–	–
	25	2.53	63.12	–	–
	50	1.39	69.70	–	–
Model 2 (P only)	0.25	–	–	26.39	5.90
	0.5	–	–	19.15	8.57
	1	–	–	16.17	14.48
	2.5	–	–	11.15	24.95
	5	–	–	9.02	40.38
	10	–	–	8.34	74.67
	25	–	–	4.29	96.00
	50	–	–	2.21	99.05
Model 3 (C/P=3/1)	0.25	7.23	1.26	47.66	16.28
	0.5	6.14	2.13	43.40	29.65
	1	5.57	3.86	35.74	48.84
	2.5	4.50	7.80	19.83	67.73
	5	4.07	14.11	13.32	90.99
	10	3.99	27.66	6.72	91.86
	25	3.96	68.64	2.80	95.64
	50	2.09	72.58	1.45	99.42
Model 4 (C/P=1/1)	0.25	97.27	19.69	85.96	18.81
	0.5	56.59	22.91	45.11	19.74
	1	42.39	34.32	31.49	27.56
	2.5	17.86	36.16	16.25	35.57
	5	10.04	40.67	10.72	46.93
	10	6.43	52.07	8.26	72.25
	25	3.76	76.18	4.38	95.90
	50	2.06	83.63	2.23	97.76
Model 5 (C/P=1/3)	0.25	6.82	3.33	93.62	14.84
	0.5	7.50	7.32	47.66	15.11
	1	6.25	12.19	26.38	16.73
	2.5	3.91	19.07	12.76	20.24
	5	6.16	60.10	12.04	38.19
	10	3.60	70.30	8.42	53.44
	25	1.99	96.92	5.92	93.66
	50	1.02	99.87	3.07	97.30

the amount of activated carbon from 0.25 to 50 g/L while keeping the other parameters constant (i.e., pH: 7.2 ± 0.2 , particle size: 5–75 μm , wastewater solution volume: 50 mL, contact time: 24 h, and agitation speed: 175 rpm). As presented in Table 4, the removal efficiency of both carbohydrate and protein increased with increasing adsorbent dosage. It was observed that the removal of protein became more efficient from the synthetic wastewater solution with increase in adsorbent dosage. The optimum adsorption dosage was determined as 25 g/L for adsorption of carbohydrate and protein and the removal percentage increased with increase in the amount of activated carbon as presented in Table 4. It could be clearly seen from the Table 4 that the individual and competitive adsorption efficiency increased with increase in adsorbent dosage from 0.25 to 50 g/L. Similar results have been reported from the equilibrium adsorption experiments with other wastewaters [15,35].

Decrease in the adsorption capacity at higher activated carbon dosages could be explained based on the ratio of the initial concentration of SMP to the available sorption sites on the activated carbon. At high carbon dosages, this ratio is higher; hence some of the adsorption sites remain unsaturated at the equilibrium state. On the other hand, at the lower activated carbon dosage, the available sites are depleted faster compared to the amount of SMP resulting in lower SMP removal efficiency. The percent adsorption values increased with increasing adsorbent dosage from 0.25 to 50.0 g/L due to the increase in availability of surface functional groups [36].

4.3. Effect of the agitation time and initial SMP concentration

A series of time controlled experiments were conducted with the initial carbohydrate and protein concentrations ranging from 50 to 200 mg/L at $23 \pm 2^\circ\text{C}$. Fig. 2 presents the amount of SMP adsorbed on activated carbon over time. The agitation time necessary to reach equilibrium was observed to be between 50 and 120 min. The sorption capacities of the activated carbon were 1.6, 2.3, and 4.5 mg/g for the carbohydrate solutions (Fig. 2a) and 2.0, 4.0, and 6.8 mg/g for the protein solutions (Fig. 2b) for the experiments conducted with the initial SMP concentrations of 50, 100, and 200 mg/L, respectively. The contact time necessary to reach equilibrium showed a direct correlation with the initial SMP concentration.

For the competitive adsorption experiments, as presented in Fig. 2c and d, the amounts of SMP fractions sorbed on activated carbon increased with time, similar to the noncompetitive adsorption experiments. However, for the competitive adsorption conditions, the sorption capacity ($q_{e,exp}$ in pseudo-first order model) decreased from 3.55 to 0.94 mg/g for carbohydrate and increased from 2.59 to 5.71 mg/g for protein with model 3 (C/P=3/1) and model 5 (C/P=1/3) wastewaters, respectively as shown in Table 5. The agitation time necessary to reach equilibrium was between 50 min and 150 min depending on the initial SMP levels and longer when protein was at a higher concentration. The solutions with lower initial SMP levels reached equilibrium faster than those with higher initial concentrations.

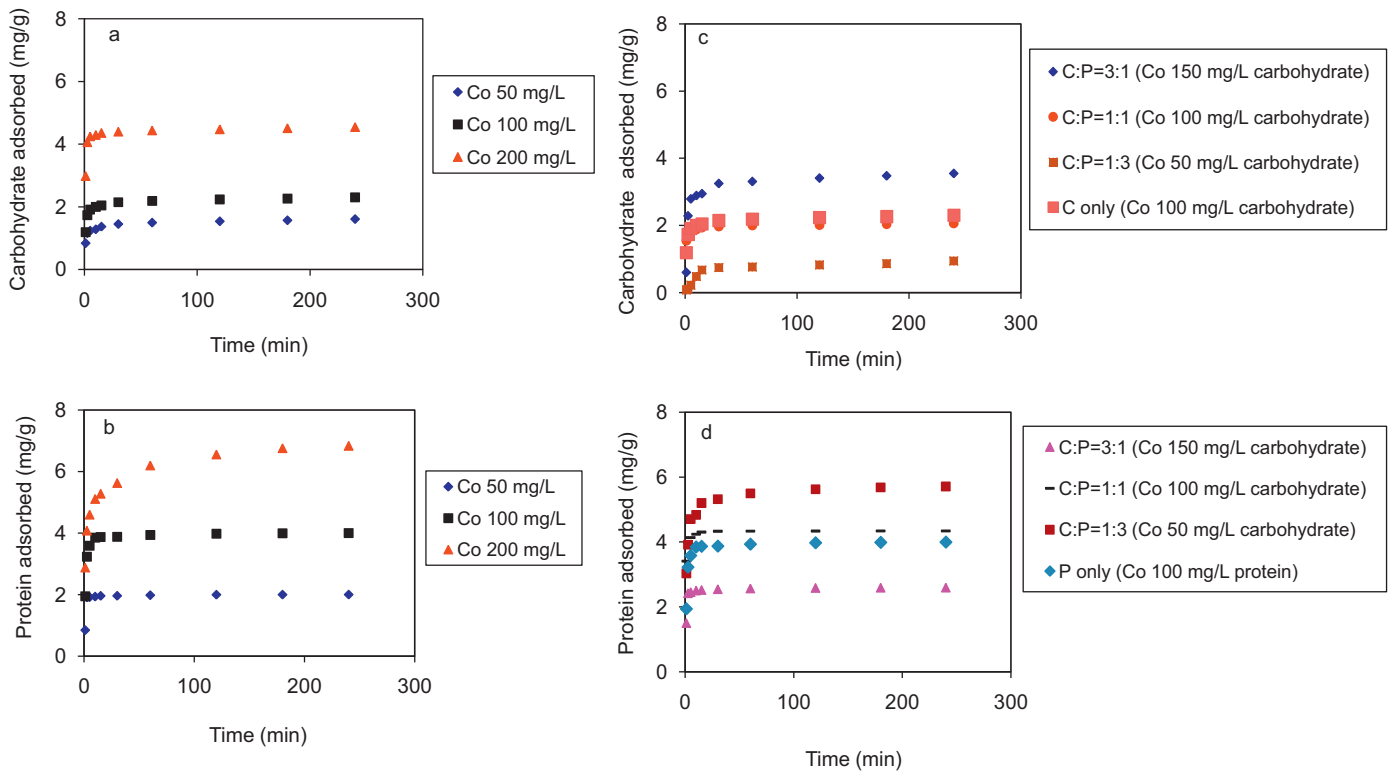


Fig. 2. Effect of contact time and initial SMP concentration on sorption capacity for individual and competitive sorption of carbohydrate and protein onto activated carbon (pH: 7.2 ± 0.2, T: 25 ± 2 °C, m_s : 25 g/L, particle size: 5–75 μm, contact time: 240 min, agitation speed: 175 rpm): (a) carbohydrate only, (b) protein only, (c) carbohydrate sorption profile under competitive conditions, (d) protein sorption profile under competitive conditions.

4.4. Kinetic models

4.4.1. Reaction-based kinetic models

The nature of sorption process depends on both physicochemical characteristics of the adsorbent and the aqueous system conditions [37]. To investigate the mechanisms of SMP sorption on activated carbon under both individual and competitive conditions, the rates of sorption were determined using the Lagergren pseudo-first order (Eq. (3)) and the pseudo-second order (Eq. (4)) kinetic models. Table 5 presents rate

constants (k_1) estimated from the linearized form of Lagergren pseudo-first order model. The sorption rate constant (k_1) was estimated as 0.0145 ± 0.0005 per min for carbohydrate and 0.019 ± 0.004 per min for protein. For the pseudo-second order kinetic model the sorption rate constant (k_2) and sorption capacity (q_e) were calculated from the linearized model graphically (i.e., from the plots of t/q_t vs. t). The estimated kinetic constants (k_2 , $q_{e,cal}$ and h) for the linear form of the pseudo-second order model at different SMP concentrations are presented in Table 5.

Table 5
Reaction-based kinetic parameters for individual and competitive carbohydrate and protein sorption onto activated carbon.

Reaction-based kinetic models	Pseudo-first order				Pseudo-second order			
	$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t$				$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \quad h = k_2 q_e^2$			
Wastewater and SMP level ^a	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (1/min)	r^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg min)	h (mg/g min)	r^2
<i>Individual adsorption of carbohydrate^b</i>								
Model 1 C = 50 mg/L	C:1.61	C:0.39	C:0.014	C:0.859	C:1.60	C:0.598	C:1.540	C:0.999
Model 1 C = 100 mg/L	C:2.30	C:0.43	C:0.015	C:0.805	C:2.30	C:0.142	C:0.753	C:0.999
Model 1 C = 200 mg/L	C:4.54	C:0.39	C:0.015	C:0.699	C:4.54	C:0.008	C:0.162	C:1.000
<i>Individual adsorption of protein^c</i>								
Model 2 P = 50 mg/L	P:2.00	P:0.13	P:0.027	P:0.784	P:2.00	P:0.067	P:0.270	P:1.000
Model 2 P = 100 mg/L	P:4.00	P:0.43	P:0.024	P:0.791	P:4.00	P:0.012	P:0.191	P:1.000
Model 2 P = 200 mg/L	P:6.83	P:2.53	P:0.019	P:0.968	P:6.89	P:0.012	P:0.564	P:0.999
<i>Competitive adsorption of carbohydrate and protein</i>								
Model 3 C = 150 mg/L	C:3.55	C:0.96	C:0.016	C:0.786	C:3.56	C:0.068	C:0.870	C:0.999
P = 50 mg/L	P:2.59	P:0.18	P:0.026	P:0.837	P:2.59	P:0.027	P:0.184	P:1.000
Model 4	C:2.06	C:0.23	C:0.014	C:0.785	C:2.06	C:0.114	C:0.483	C:0.999
C = 100 mg/L	P:4.34	P:0.19	P:0.049	P:0.889	P:4.34	P:0.002	P:0.045	P:1.000
P = 100 mg/L								
Model 5 C = 50 mg/L	C:0.94	C:0.54	C:0.012	C:0.759	C:0.96	C:14.83	C:13.80	C:0.995
P = 150 mg/L	P:5.71	P:1.20	P:0.022	P:0.904	P:5.73	P:0.009	P:0.287	P:0.999

^a C: carbohydrate, P: protein.

^b Model 1 wastewater was prepared to contain carbohydrate at three different concentrations.

^c Model 1 wastewater was prepared to contain protein at three different concentrations.

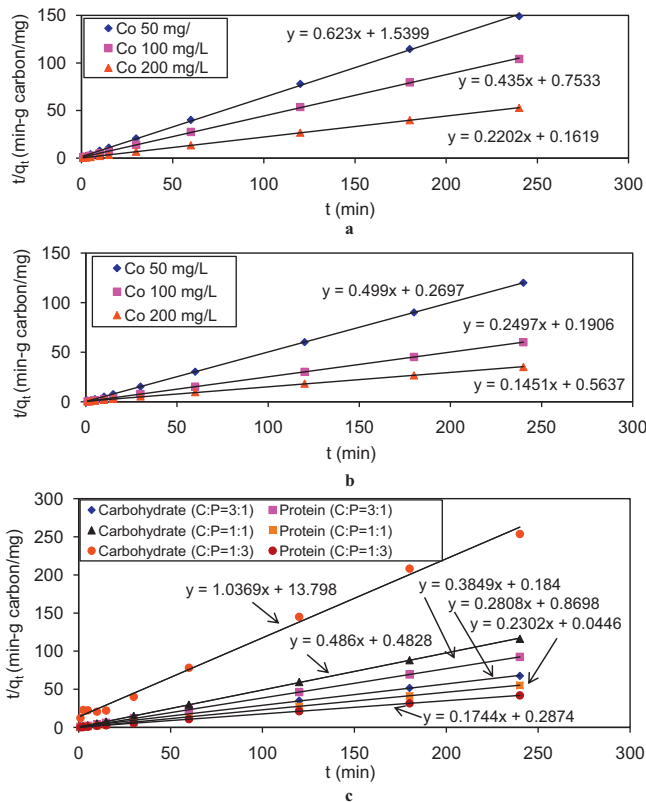


Fig. 3. Adequacy of the pseudo-second order kinetic models for SMP sorption (pH: 7.2 ± 0.2 , $T: 25 \pm 2^\circ\text{C}$, $m_s: 25\text{ g/L}$, particle size: $5\text{--}75\ \mu\text{m}$, contact time: 240 min, agitation speed: 175 rpm): (a) individual carbohydrate adsorption, (b) individual protein adsorption, (c) competitive carbohydrate and protein adsorption.

Fig. 3a–c compares the experimental data and model for the pseudo-second order kinetic model for the synthetic wastewater solutions with initial concentrations of 50–200 mg/L. The values estimated for k_2 , $q_{e,\text{cal}}$ and h with the linear form of the pseudo-second order model were similar to the experimental observations. The relatively high values of r^2 (greater than 0.90) confirm that the sorption kinetics followed a pseudo-second order mechanism for both individual carbohydrate and protein adsorption. The results indicate that the sorption process is controlled by chemisorption [38].

Under noncompetitive sorption conditions, amount of SMP adsorbed increased approximately from 1.61 to 4.54 mg/g for carbohydrate and from 2.00 to 6.83 mg/g for protein when the initial SMP concentration increased from 50 mg/L to 200 mg/L. However, under competitive sorption conditions; the amount of carbohydrate adsorbed increased from 0.94 mg/g to 3.55 mg/g when the initial C/P ratio increased from 1/3 to 3/1. The amount of protein adsorbed increased from 2.59 mg/g to 5.71 when the initial C/P ratio decreased from 3/1 to 1/3 as presented in Table 5 (model 3 and model 5 wastewater) and Fig. 3. Removal of carbohydrate and protein from the model wastewaters were directly correlated with the initial SMP concentrations.

4.4.2. Diffusion-based kinetic models

The parameters calculated from the diffusion-based models are presented in Table 6. The values of Weber–Morris intraparticle diffusion rates decreased from 0.0185 to 0.0151 $\text{mg/g min}^{1/2}$ for carbohydrate and increased from 0.004 to 0.134 $\text{mg/g min}^{1/2}$ for protein with increase in initial concentrations from 50 to 200 mg/L under noncompetitive conditions. However, the Weber–Morris intraparticle diffusion rate decreased from 0.043 to 0.020 $\text{mg/g min}^{1/2}$ for carbohydrate and increased from 0.006 to

0.044 $\text{mg/g min}^{1/2}$ for protein under competitive adsorption conditions. The intraparticle diffusion coefficients, k_{id} , and external mass transfer coefficient, k_f , decreased for carbohydrate and increased for protein with increase in the initial SMP concentrations as presented in Table 6.

4.5. Adsorption isotherm models for equilibrium conditions

To determine the noncompetitive sorption isotherms, initial concentrations of carbohydrate or protein were varied while the amount of adsorbent in each sample was kept constant. The Langmuir adsorption isotherms of carbohydrate and protein under noncompetitive conditions are presented in Fig. 4a and b. The adsorption isotherms of carbohydrate and protein under competitive conditions (i.e., when both SMP fractions are present) are presented in Fig. 4c. The adsorption constants for each component estimated by Langmuir and Freundlich models are presented in Table 7. Based on the regression coefficients, the Langmuir model exhibited a better fit for the adsorption data for both carbohydrate and protein ($r^2 > 0.90$).

Under the competitive sorption conditions, the time required to reach equilibrium become longer due to near surface interactions and molecular reconfiguration at the surface to minimize surface energy. The difference in sorption rates also significantly affected the sorption of glucose and protein when both compounds were present. These results may be due to significantly different molecular size and solubility characteristics of glucose and BSA.

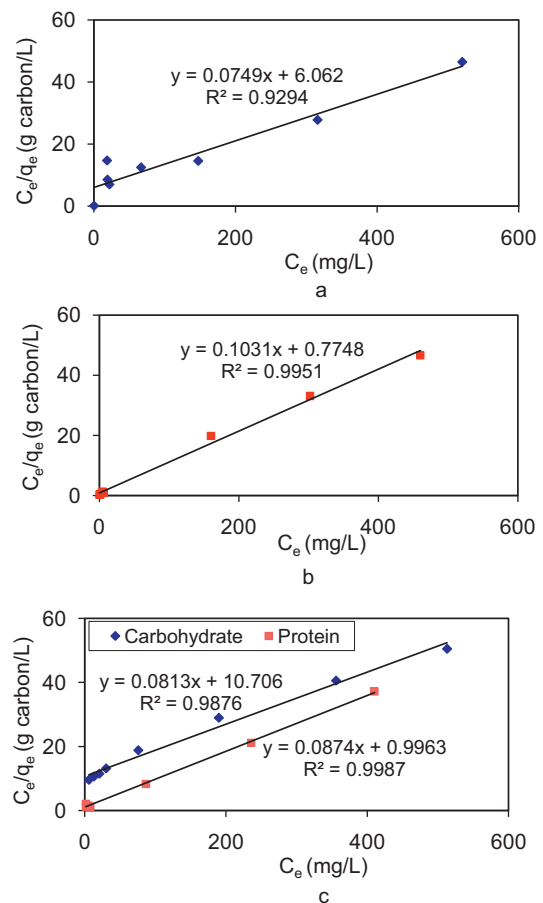


Fig. 4. Langmuir adsorption isotherms for carbohydrate and protein under noncompetitive and competitive sorption conditions (pH: 7.2 ± 0.2 , $T: 23 \pm 2^\circ\text{C}$, $m_s: 25\text{ g/L}$, contact time: 24 h, agitation speed: 175 rpm): (a) carbohydrate under noncompetitive sorption conditions, (b) protein under noncompetitive sorption conditions, (c) carbohydrate and protein under competitive sorption conditions.

Table 6
Diffusion-based kinetic parameters for individual and competitive carbohydrate and protein sorption onto activated carbon.

Diffusion-based kinetic models	External diffusion model		Weber–Morris intraparticle diffusion model	
Parameters	$\ln \frac{C_0}{C_t} = -k_f \frac{A}{V} (t) \left[\frac{A}{V} = 3 \frac{m}{\rho d} \right]$		$q_t = k_{id}(t)^{1/2}$	
Wastewater and SMP level ^a	$k_f (\times 10^{-6})$ (cm/s)	r^2	k_{id} (mg/g min ^{1/2})	r^2
<i>Individual adsorption of carbohydrate^b</i>				
Model 1 C = 50 mg/L	C:80.0	C:0.539	C:0.0185	C:0.944
Model 1 C = 100 mg/L	C:80.0	C:0.325	C:0.0195	C:0.917
Model 1 C = 200 mg/L	C:53.3	C:0.184	C:0.0151	C:0.988
<i>Individual adsorption of protein^c</i>				
Model 2 P = 50 mg/L	P:0.13	P:0.794	P:0.004	P:0.907
Model 2 P = 100 mg/L	P:0.11	P:0.781	P:0.012	P:0.930
Model 2 P = 200 mg/L	P:5.33	P:0.786	P:0.134	P:0.932
<i>Competitive adsorption of carbohydrate and protein</i>				
Model 3 C = 150 mg/L	C:80.0	C:0.404	C:0.043	C:0.852
P = 50 mg/L	P:0.11	P:0.772	P:0.006	P:0.897
Model 4 C = 100 mg/L	C:53.3	C:0.206	C:0.009	C:0.961
P = 100 mg/L	P:0.19	P:0.868	P:0.001	P:0.894
Model 5 C = 50 mg/L	C:1.07	C:0.619	C:0.020	C:0.966
P = 150 mg/L	P:8.00	P:0.827	P:0.044	P:0.932

^a C: carbohydrate, P: protein.

^b Model 1 wastewater was prepared to contain carbohydrate at three different concentrations.

^c Model 2 wastewater was prepared to contain protein at three different concentrations.

Table 7
Comparison of the individual and competitive Langmuir and Freundlich adsorption constants for carbohydrate and protein.

	Q_0 (mg/g)	b (L/mg)	r^2
<i>Single-component Langmuir model</i>			
Carbohydrate	13.35	0.454	0.929
Protein	9.70	0.079	0.995
<i>Multi-component Langmuir model</i>			
Carbohydrate	12.30	0.870	0.988
Protein	11.44	0.087	0.999
	k_f (mg/g)	n	r^2
<i>Single-component Freundlich model</i>			
Carbohydrate	1.30	3.13	0.753
Protein	2.22	3.72	0.865
<i>Multi-component Freundlich model</i>			
Carbohydrate	0.26	1.65	0.986
Protein	1.42	2.53	0.798

5. Conclusions

Adsorption characteristics of soluble microbial products (as carbohydrate and protein) on activated carbon were studied under competitive and noncompetitive sorption conditions. The relatively significant effect of particle size on sorption of protein indicates that protein may be adsorbed as a single layer on the carbon surface. For the carbohydrate, the increase in particle size did not decrease the sorption efficiency significantly. The equilibrium sorption levels of carbohydrate and protein were significantly affected by the presence of the second SMP component in the solution. Activated carbon effectively removed both carbohydrate and protein fractions; however, sorption of protein was significantly better than that of carbohydrate in all cases.

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