Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1087884

57 (2016) 16404–16414
July

Taylor & Francis
Taylor & Francis Group

Dynamic behavior of the adsorption, activated sludge and combined activated sludge-adsorption process for treatment of cheese whey wastewater

Fatemeh Aghili, Ali Asghar Ghoreyshi*, Ahmad Rahimpour, Mostafa Rahimnejad

Chemical Engineering Department, Babol University of Technology, Shariati Street, Babol, Iran, Tel. +98 111 3234204; Fax: +98 111 3234204; email: aa_ghoreyshi@nit.ac.ir (A.A. Ghoreyshi)

Received 1 March 2015; Accepted 2 August 2015

ABSTRACT

Treatment of cheese whey wastewater (CWW) in terms of chemical oxygen demand (COD) removal by adsorption, activated sludge (AS), and combination of these two processes was investigated. The equilibrium and kinetic data for adsorption of organics available in CWW onto three types of powdered activated carbons (PACs) were successfully described by hybrid Langmuir–Freundlich and pseudo-second-order models, respectively. The results indicated that AS–PAC combined system outperformed individual AS process in different COD concentrations. The most significant result was observed at the 7,500 mg/L COD concentration with the broom sorghum PAC (BSPAC) with a PAC dose of 4 g/L which could improve COD removal efficiency from 52.3% for AS to 63.8% for AS–PAC system. The most substantial result in this study was demonstration of the PAC bioregeneration mechanism in AS–PAC process. Dynamic behavior of the AS, PAC adsorption, and AS–PAC process was modeled in terms of a set of coupled differential equations. An optimization procedure was followed to obtain the model adjustable parameters that showed the desorption index (K_{des}) for AS–PAC process was more than the value that was obtained for adsorption process. Also, in AS–PAC process, the maximum specific adsorption capacity of PAC decreased.

Keywords: Adsorption; Activated sludge; Cheese whey wastewater; Biodegradation; AS–PAC process

1. Introduction

With the growing industrialization trends and density of population in the last decades, wastewater treatment has become a noticeable environmental issue. Within the food-processing industry, the dairy industry is one of the major contributors to wastewater generation in terms of both organic load value and effluent volume [1,2]. Thus, the dairy industry is forced to treat its effluents effectively. The challenge is to find cost-efficient and environmentally sustainable approaches to enable water reuse, byproduct disposal, and waste management.

Cheese whey is produced as a byproduct during cheese manufacturing, which contains carbohydrates, proteins, and fats that results in a high organic load [3]. Cheese whey wastewater (CWW) mainly consists of raw materials, carried into the wastewater during handling, processing, and cleaning the materials is classified as a high-strength wastewater in terms of high

---

*Corresponding author.

chemical oxygen demand (COD) (800–77,000 mg/L) and high biochemical oxygen demand (BOD) (600–16,000 mg/L) [4–7]. Organic matters constitute the main emission load of dairy wastewater with high BOD and COD. Dairy effluents with such high organic load could not be simply treated based on biological processes. Many authors reported about treatment of dairy wastewater by anaerobic biological methods such as upflow anaerobic sludge and anaerobic filters [8]. Frigon et al. [9] applied anaerobic and aerobic steps in a single digester for treatment of CWW. It was found that a total cycle time of at least three days was required to obtain satisfactory COD removal (97%) and residual COD (33 mg/L).

Complete removal of all organic matters needs complementary post treatment such as coagulation, electrochemical treatment, and adsorption [10,11].

Activated sludge (AS) treatment is a feasible option to treat highly biodegradable wastewater [12]. Advanced treatment requires removing nonbiodegradable, toxic or inhibitory organics, and some heavy metals [13,14]. The ability of powdered activated carbon (PAC) in removal of refractory organic compounds has been demonstrated [15]. The addition of PAC to AS system increases the contact time between biomass and toxic low biodegradable compounds due to adsorption onto the PAC surfaces. This improves growth of biofilm onto the PAC surfaces and can enhance the microbial specific population, which can effectively contribute to the degradation of the toxic compounds [16]. The transformation of sludge into a PAC suitable for liquid phase application may offer reducing of the sludge volume. Thus, the hybrid process containing PAC and AS, could remove organic compounds more efficiently than would be expected from either biodegradation or adsorption alone. Ferro Orozco et al. [17] showed that the main effect of PAC on the growth kinetics is to act as a buffer of substrate (cheese whey) concentration changes. Indeed, the stability of environmental conditions within the combined AS–PAC process is better maintained due to the buffering function of substrate in the presence of PAC. Ferro Orozco et al. [17] also developed a simplified model of the effect of PAC on the bioavailability of the growth substrate. They assumed that the adsorption process can be represented by the Langmuir adsorption isotherm model and the uptake of the substrate by micro-organisms follows Monod type kinetics. They also estimated the coefficients of the mathematical model using the software package Gepasi 3. However, the exact role of PAC in the AS process has not yet been elucidated.

Some authors have reported some qualitative indications for the occurrence of bioregeneration [18,19]. Bioregeneration of an adsorbent takes place as a result of interaction between micro-organisms and adsorbed molecules. On the other hand, biomass is degrading organic matters in bulk liquid; first the adsorbed material desorbs, then diffuses out of the carbon, and finally biodegradation takes place [20]. However, the mechanism of bioregeneration is not fully understood yet and a few attempts were made to elaborate the theoretical aspects of AS–PAC process based on a sophisticated model. Therefore, a major task in this area may be the development of a mathematical model to describe quantitative correlation between the kinetics parameters and bioregeneration of PAC in AS–PAC process. Most of the above-addressed articles have studied the incorporation of PAC in AS systems for the treatment of complex liquid waste containing nonbiodegradable compounds and toxic or inhibitory substances to improve the performance treatment. However, information about the effect of AS–PAC process for the treatment of biodegradable wastewaters is limited. Therefore, the present study was aimed (i) to determine the adsorption kinetic and equilibrium isotherm of the growth substrate (cheese whey) onto PAC in the absence of biomass and find optimum concentration of three kinds of PACs for organic matters removal, (ii) to analyze the effect of optimum dose of PAC on the growth of AS and removal of organic matters in different initial load of COD, (iii) to describe the performance of the individual biodegradation and adsorption as well as combined biodegradation–adsorption processes through suitable mathematical models, and (iv) to demonstrate correlation between the kinetics parameters and bioregeneration of PAC by a developed mathematical model. Also, we employed the intelligent algorithm optimization (particle swarm optimization) that could help us to extract optimum kinetics parameters.

For this purpose, three types of low-cost synthetic PACs prepared in our laboratory from agricultural waste were applied and cheese whey with high-load COD was used as a wastewater.

2. Materials and methods

2.1. Wastewater source and sludge

CWW used in this study was collected from the dairy plant of Kalleh Company, Amol, Iran. The COD of the effluent varied between 47,400 and 69,000 mg/L. The typical values for other physicochemical parameters were as follows: total suspended solids (TSS): 3,970 ± 80 mg/L; total dissolved solids: 3,720 ± 10 mg/L; total Kjeldahl nitrogen: 3,650 mg/L; ammonium

($N\text{-}NH_4^+$): 45.1 mg/L; conductivity: 7.51 ± 0.2 mS/cm; and pH: 4.31 ± 0.07. The whey sample was stored at 4°C to avoid acidification and changes in chemical composition.

The AS used in all experiments was also harvested from the aerobic wastewater treatment plant of the same dairy plant. It was acclimatized to treat high-load CWW in a fed-batch reactor.

2.2. PAC characterization

Three kinds of available PACs prepared from agricultural solid wastes, i.e. broom sorghum (BSPAC), rice husk (RHPAC), and carbon molecular sieves (CMSPAC) were used [21,22]. Some characteristics of the used PACs are shown in Table 1. The textural properties of all PACs including Brunauer–Emmet–Teller (BET) surface area, pore size distribution, and total pore volume were determined, using N_2 adsorption/desorption isotherm at 77 K in a surface area analyzer (Belsorp-mini II, Japan). The surface area (S_{BET}) was calculated by the BET equation. The pore size distribution and the average pore diameter of the adsorbent were determined by the Barrett–Joyner–Halenda method. Pore volume (V_{total}) was obtained according the *t*-plot method.

2.3. Adsorption isotherm and kinetics and COD removal in batch reactor by PAC

To determine the optimum dosage of PACs 2, 4, 8, and 12 g/L of each PAC (BSPAC, RHPAC, and CMSPAC) and 50 mL of diluted CWW at a constant COD (6,200 ± 100) and pH (7.00 ± 0.05) were mixed in Erlenmeyer flasks, which were placed in an incubator shaker at 180 rpm and constant temperature (22 ± 2°C). For determination of adsorption isotherm, the adsorbent was separated from the CWW after 8 h (adequate time to make sure that the equilibrium was reached) and analyzed to determine COD using spectrophotometer model AL250 AQUALYTIC® Germany. For equilibrium experiments, the PAC dose of 4 g/L as the optimum dose at different initial COD concentrations (COD_0 = 1,300–11,000 mg/L) of CWW were used. The amount of organic matters adsorbed at equilibrium, q_e (mg/g), can be calculated from the following equation (Eq. (1)):

$$q_e = \frac{(COD_0 - COD_e)V}{m_{PAC}} \tag{1}$$

where COD_0 (mg/L) and COD_e (mg/L) are the initial and equilibrium COD concentrations of liquid phase, respectively. V (L) is the volume of the solution and m_{PAC} (g) is the mass of the PAC used in the experiment.

For the kinetic test, measurement of COD took place at 10, 30, 60, 120, 180, and 240 min. The uptake of the adsorbate at time t (min), q_t (mg/g), was calculated by the following equation (Eq. (2)):

$$q_t = \frac{(COD_0 - COD_t)V}{m_{PAC}} \tag{2}$$

where COD_t (mg/L) is the concentration of the adsorbate in solution at time t.

Note that for all experiments, the initial pH was set to 7.00 ± 0.05 by adding a few drops of a concentrated NaOH solution.

2.4. Growth of biomass and COD removal in batch reactor by AS

In order to study the COD removal and the effect of the initial COD concentration on the growth kinetics of AS, batch assays were performed in 500-mL aerated vessels. Three initial COD concentrations (COD_0) were used; i.e. 2,500, 5,000, and 7,500 mg/L. In all cases, the initial biomass concentration, (TSS), measured based on the 2540D Standard Method APHA [23], was 775 ± 30 mg/L. During the experiments, dissolved oxygen concentration, measured using oxygen

Table 1
Textual characteristics BSPAC, RHPAC, and CMSPAC

PAC	Base material	Activation agent	S_{BET} (m^2/g)	V_{total} (cm^3/g)	Average pore diameter (nm)	Micropores (%)
BSPAC	Broom sorghum	$ZnCl_2$	1121.3	0.5668	2.0219	30.71
RHPAC	Rice husk	$ZnCl_2$	757.3	0.3769	1.9910	75.08
CMSPAC[a]	Broom sorghum	$ZnCl_2$	815.6	0.3001	1.4717	60.53

[a] Chemical vapor deposition of PAC with methane.

electrode (OXPB-11) LOVIBOND® water testing method, was kept above 5.2 mg/L. All experiments were performed at room temperature (22 ± 2˚C), and COD and TSS were measured every 2-h period, for 24 h.

For each experiment, the biomass yield $\left(Y_{\mathrm{TSS/COD}}\right)$ was obtained from the slope of the plot of TSS vs. the COD concentration. The observed specific growth rate (μ_{obs}) (h^{-1}) was calculated from the slope of the linear part of the plot of $\ln \mathrm{TSS}$ as a function of time.

2.5. Growth of biomass and COD removal in the batch reactor by hybrid AS–PAC system

Experiments for assessment of biomass growth and COD removal in the AS–PAC batch reactor were carried out based on the method described in the previous section, with an exception that PAC was added. Among three kinds of PACs used in pure adsorption study, the one with the best results was selected for application in AS–PAC process.

3. Results and discussion

3.1. Adsorption studies and COD removal by PAC in the absence of biomass

The effect of adsorbent dosage on the adsorption of organic matters by BSPAC, RHPAC, and CMSPAC was evaluated at constant initial COD of 6,200 mg/L. Table 2 indicates that the COD removal efficiency, determined by Eq. (3), enhanced with increase in PAC dosage whilst the equilibrium uptake was decreased. An increase in the COD removal with the increase in adsorbent dosage can be attributed to greater availability of the exchangeable sites or surface area; however, decrease in the effective surface area for the adsorption due to the partial aggregation of PAC resulted in a decrease in the amount of adsorption. Fig. 1 depicted the variation of adsorption capacity and removal efficiency vs. adsorbent dosage and the optimum dosage value is generally where two curves intersect each other. Therefore, the optimum doses of the BSPAC, RHPAC, and CMSPAC in removing organic matters from CWW were 4 g/L corresponding to 43, 38, and 35% COD removal efficiency, respectively.

$$\text{Percent COD removal} = \frac{(\mathrm{COD}_0 - \mathrm{COD}_e)}{\mathrm{COD}_0} \times 100^{\sim} \tag{3}$$

The adsorption isotherm indicates the distribution of the adsorbate between the liquid and the solid phases at the equilibrium state. To describe this relationship, three isotherm equations, namely Langmuir, Freundlich, and Langmuir–Freundlich, given by Eqs. (4)–(6), respectively, were used to fit the experimental data for CWW adsorption onto BSPAC, RHPAC, and CMSPAC.

$$q_e = \frac{q_{\max} K_L \mathrm{COD}_e}{1 + K_L \mathrm{COD}_e} \tag{4}$$

where $q_{\max}$ (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant related to the free energy of the adsorption

$$q_e = K_F \mathrm{COD}_e^{1/n} \tag{5}$$

where K_F ((mg/g)/(L/mg)$^{1/n}$) is the Freundlich constant related to the adsorption capacity and n (dimensionless)

Table 2
Effect of adsorbent dosage on adsorption capacity and COD removal, COD_0 = 6,200 mg/L

Activated carbon type	Dose (g/L)	q (mg/g)	COD removal efficiency (%)
BSPAC	2	1080	34.86
	4	662.5	42.71
	8	356.25	45.93
	12	246.67	47.74
RHPAC	2	990	31.93
	4	592.5	38.2
	8	323.75	41.75
	12	227.5	44.07
CMSPAC	2	900	28.92
	4	550	35.33
	8	303.75	39.1
	12	212.5	41.11

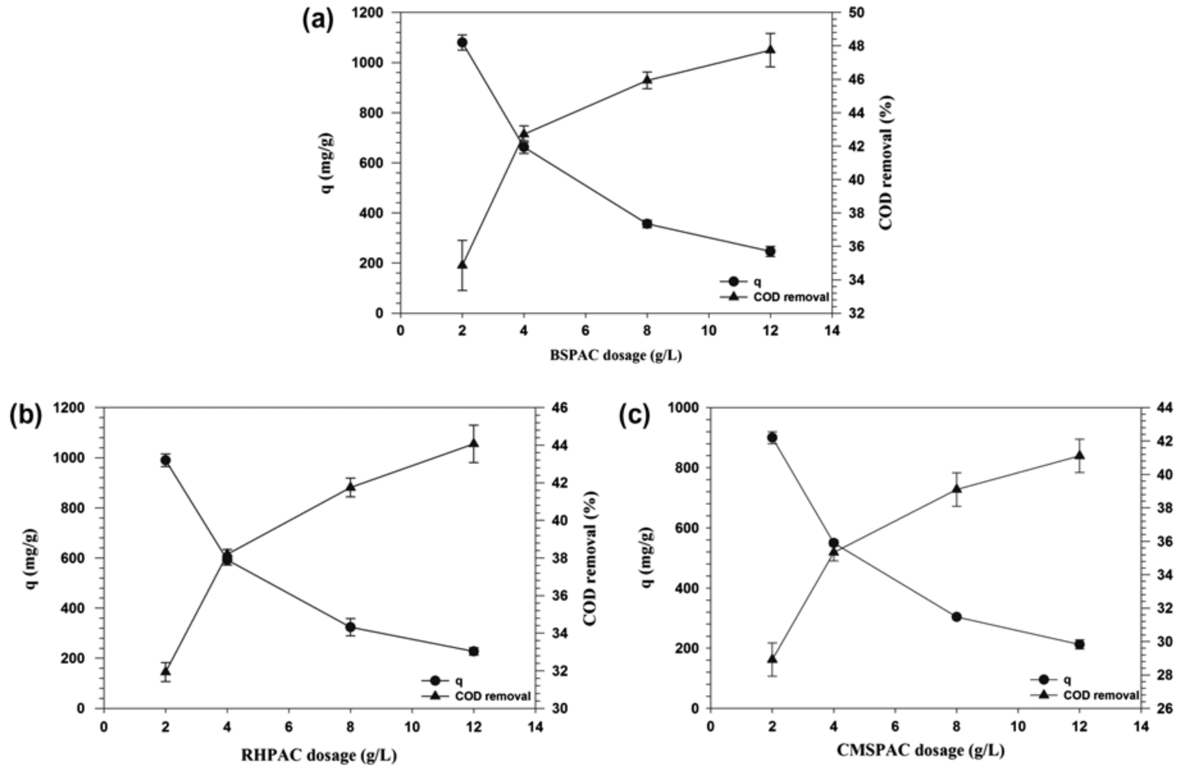

Fig. 1. Effect of adsorbent dosage on adsorption capacity and COD removal (a) BSPAC, (b) RHPAC, and (c) CMSPAC, COD_0 = 6,200 mg/L.
Note: Bars indicate the standard deviation.

is also the Freundlich constant related to the adsorption intensity, which varies with the heterogeneity of the material.

$$q_e = \frac{q_{\max}(K_{LF}COD_e)^b}{1 + (K_{LF}COD_e)^b} \tag{6}$$

The values of K_{LF} (L/mg) and b (dimensionless) are the Langmuir–Freundlich constants, which indicate the affinity between the adsorbate and adsorbent and heterogeneity of the adsorbent sites, respectively.

The experimental isotherms along with fitted model isotherms have been shown in Fig. 2. As can be seen in Fig. 2, the Langmuir–Freundlich model can represent the equilibrium data for three kinds of PACs reasonably well. The model parameters recovered from nonlinear fit of experimental data to the model equations are given in Table 3. The determination coefficient parameter R^2 values for the Langmuir, Langmuir–Freundlich, and Freundlich isotherms as a measure of degree of fitness are also listed in Table 3. By comparing the R^2 values, it may be concluded that the Langmuir–Freundlich isotherm generally represents the best fit for the equilibrium adsorption of CWW components onto BSPAC, RHPAC, and CMSPAC. This may be due to the high adsorbate concentrations. At high adsorbate concentrations, it predicts the monolayer sorption capacity characteristics of the Langmuir isotherm, while at low adsorbate concentrations, it effectively reduces to a Freundlich isotherm and thus did not obey the Henry's Law [24].

Table 3 shows that BSPAC has higher adsorption capacity compared to RHPAC and CMSPAC. A high $q_{\max}$ value indicated a high affinity of the CWW components for binding to the adsorbent surface, which might ascribe the higher surface area of BSPAC (1,121.3 m^2/g) compared to that of RHPAC (757.3 m^2/g) and CMSPAC (815.6 m^2/g). Similar results were reported by Kushwaha et al. [1] for the adsorption of organic matters onto commercial activated carbon and bagasse fly ash. Hence, BSPAC was selected as the best adsorbent for the combined AS–PAC study due to its better performance compared to two other PACs.

Pseudo-first-order (Eq. (7)) and pseudo-second-order (Eq. (8)) models were employed to test their validity with the kinetic experimental adsorption data.

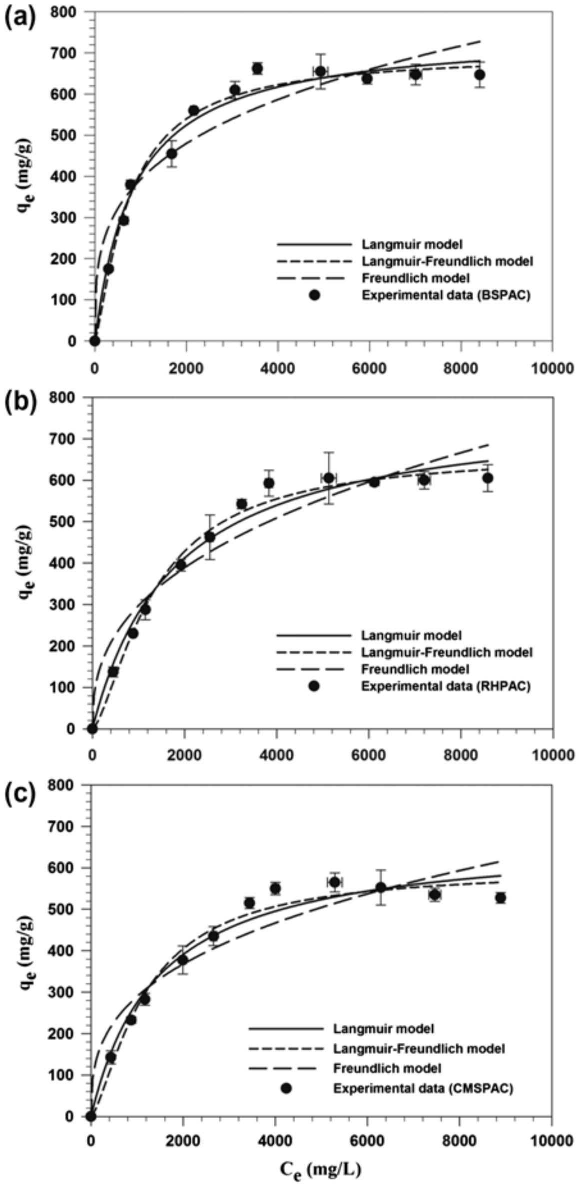

Fig. 2. Equilibrium isotherms for the adsorption of CWW by 4 g/L (a) BSPAC, (b) RHPAC, and (c) CMSPAC, COD_0 = 1,300–11,000 mg/L.
Note: Bars indicate the standard deviation.

Table 3
Isotherm parameters for the treatment of CWW by 4 g/L BSPAC, RHPAC, and CMSPAC, COD_0= 1,300–11,000 mg/L

PAC type	BSPAC	RHPAC	CMSPAC
Langmuir			
$q_{\max}$(mg/g)	729.167	728.010	662.714
K_L (L/mg)	0.0012	0.0006	0.0007
R^2	0.9816	0.9799	0.9727
Freundlich			
$1/n$	0.2892	0.3882	0.3451
K_F ((mg/g)/(L/mg)$^{1/n}$)	53.3165	20.3483	26.7109
R^2	0.923	0.9282	0.9151
Langmuir–Freundlich			
$q_{\max}$ (mg/g)	699.498	667.021	598.281
K_L (L/mg)	0.0013	0.0007	0.0008
b	1.2583	1.4639	1.4067
R^2	0.9853	0.9898	0.9811

$$q_t = \left(1 - e^{-k_1 t}\right) \tag{7}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{8}$$

where k_1 (min^{-1}) and k_2 ((g/mg) (min^{-1})) are the rate constants of pseudo-first-order and pseudo-second-order adsorptions, respectively.

Fig. 3 shows the kinetic data and model-fitted curves for adsorption of organic matters onto three kinds of PACs. It can be seen that pseudo-second-order model fit the data quite well. It is thus impelling to say that chemisorption is dominant and controls the adsorption. According to Liu et al. [25], the pseudo-second-order model is suitable for the adsorption of lower molecular weight adsorbate such as organic matters on smaller adsorbent particles. The parameters for pseudo-second-order model, obtained by nonlinear regression are summarized in Table 4.

Table 4
Kinetic parameters for the adsorption from CWW onto 4 g/L BSPAC, RHPAC, and CMSPAC, COD_0 = 6200 mg/L

PAC type		Pseudo-first-order			Pseudo-second-order		
	$q_{e,\exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2, 10^4 (g/mg) (min^{-1})	R^2
BSPAC	662.5	621.0972	0.1355	0.9843	651.9805	3.7685	0.9968
RHPAC	592.5	552.772	0.1652	0.9852	575.1972	5.7736	0.9962
CMSPAC	550	517.6126	0.1389	0.9789	544.2804	4.5013	0.9943

The adsorption process of the adsorbate molecules from the bulk liquid phase onto the adsorbent surface is presumed to involve three stages that could be described according to kinetic data presented in the Fig. 3; (stage 1) is demonstrated in the curve with a sharp slope at the first 15 min of process which shows mass transfer of the adsorbate molecules across the external boundary layer near the adsorbent surface; (stage 2) after accumulation of adsorbed molecules on the adsorbent surface, intraparticle diffusion occurs within the pores of the adsorbent between 15 and 120 min of process with a slower rate; (stage 3) adsorption into interior sites on the surface which leads to the saturation of interior active sites equilibrium. In this stage that begins after 2 h of process, the adsorption curves become flat. These three stages are generally observed in the kinetic study of any liquid adsorption.

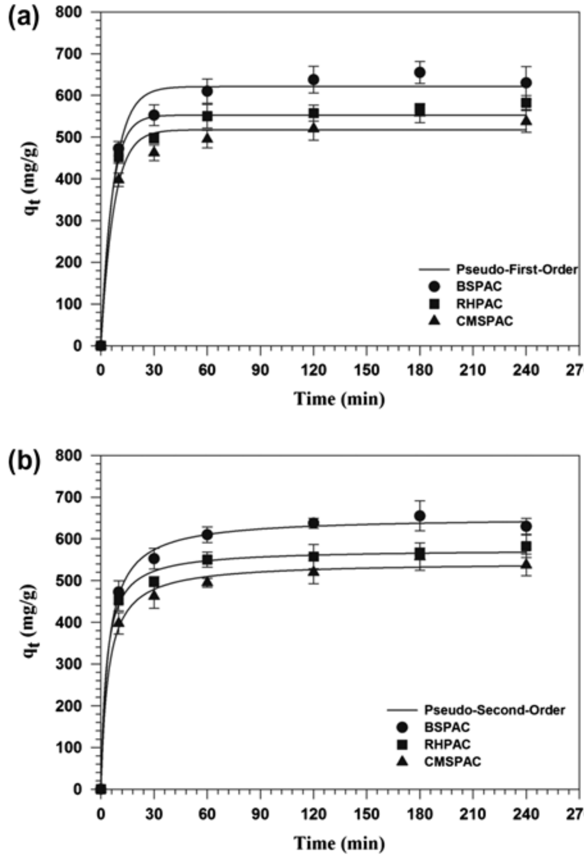

Fig. 3. Effect of contact time on the COD removal of CWW by 4 g/L BSPAC, RHPAC, and CMSPAC. Lines indicate the (a) pseudo-first-order and (b) pseudo-second-order model, $COD_0 = 6{,}200$ mg/L.
Note: Bars indicate the standard deviation.

3.2. *Effect of PAC on the biomass growth kinetics and COD removal*

The kinetics of biomass growth as well as COD removal were evaluated in the presence of BSPAC, in a series of batch experiments. For this purpose, 4 g/L BSPAC was added in a batch aeration vessel in different COD concentrations (2,500, 5,000, and 7,500 mg/L) and the COD concentration change was periodically measured. Fig. 4 shows the COD and TSS as a function of time (with and without PAC addition in different initial COD concentrations). During the first 4 h, a lag phase was observed. After the lag phase, TSS increased and the exponential growth phase ended at 16 h.

COD reduction percentages as well as biokinetic parameters, $Y_{TSS/COD}$ and μ_{obs}, in the system with and without PAC are included in Table 5. The most significant result was observed at the concentration of 7,500 mg/L COD, having 52.27 and 63.73% of COD removal after 24 h by AS and AS–PAC processes, respectively. The superior performance of AS–PAC process may be due to its better stability against the shock loading of organic matters, and this result agrees with those reported by Widjaja et al. [26]. According to Fig. 4(a), (c), and (e), during the initial hours of process, COD was almost constant in the absence of PAC; however, in the AS–PAC system, Fig. 4(b), (d), and (f), a fast decrease in COD level was observed at this stage because the adsorption rate considerably surpassed the biodegradation rate. The primary adsorption equilibrium was reached when the rates of adsorption and biodegradation were comparable. At the last stage, it seems that the process was dominated by the biodegradation, rather than adsorption. This might be due to desorption of adsorbed materials from the pores, which led to PAC regeneration. As a consequence, the adsorbed organics are desorbed because of the concentration gradient between the BSPAC surface and bulk liquid. This mechanism was also recommended by Aktas and Cecen [27]. The calculated biomass yield, YTSS/COD, was improved with the addition of PAC. Also, as Table 5 shows, the impact of PAC present on the biomass yield in AS process increased with COD concentration. The observed specific growth rate, μ_{obs}, also increased as the initial COD concentration increased and decreased when the PAC was added in the batch aeration vessel. The lack of substrate due to the adsorption onto PAC probably imposes a limitation on bacterial growth.

3.3. *Kinetic model for microbial growth with and without PAC*

In previous Section (3.1), it was demonstrated that the Langmuir model can represent the sorption of

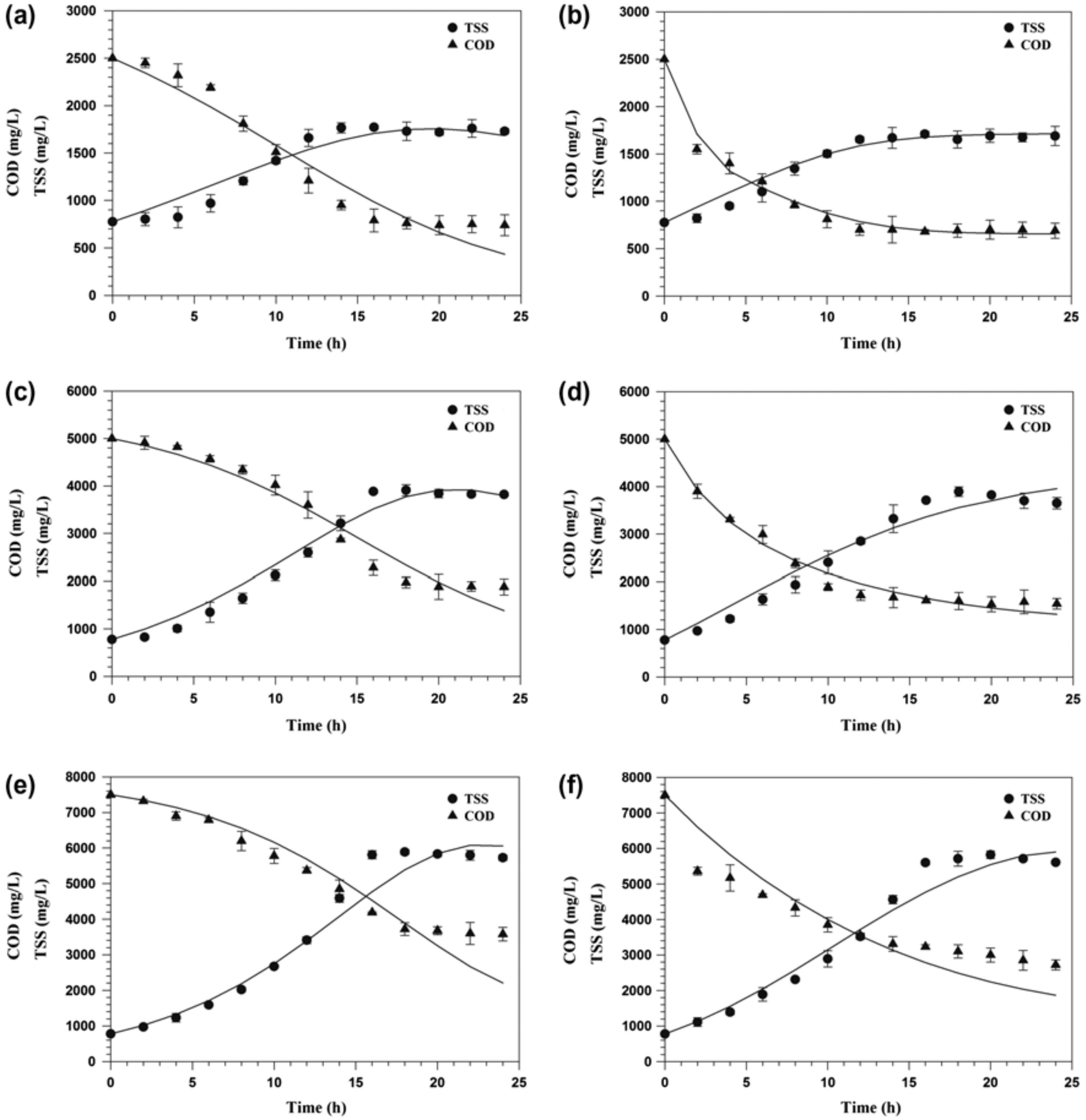

Fig. 4. COD concentration (COD) and biomass concentration (TSS) as a function of time; (a and b) with initial concentration of COD (2,500 mg/L) for AS and AS–PAC process; (c and d) with initial concentration of COD (5,000 mg/L) for AS and AS–PAC process; (e and f) with initial concentration of COD (7,500 mg/L) for AS and AS–PAC process. In all cases, the initial biomass concentration (TSS) was 775 mg/L. Lines indicate the proposed model (Eqs. (13)–(15)).
Note: Bars indicate the standard deviation.

organic matters from CWW onto the PAC. The adsorption process can be considered as the result of the substrate adsorption, COD, onto free carbon (C_F) to yield combined carbon C_C and desorption of substrate from C_C to bulk liquid based on the following reversible reaction:

$$\alpha\mathrm{COD} + C_F \underset{\text{Desorption }(K_{\mathrm{des}})}{\overset{\text{Adsorption }(K_{\mathrm{ads}})}{\rightleftarrows}} C_C \tag{9}$$

where α (mg/g) is the amount of substrate adsorbed per gram of PAC, and K_{ads} (L/mg) (h^{-1}) and K_{des} (h^{-1}) are the adsorption and desorption rate constants, respectively. The change in the concentration of the species involved in PAC process can be given by the following equation:

$$\frac{\mathrm{dCOD}}{\mathrm{d}t} = -\alpha(K_{\mathrm{ads}} \cdot \mathrm{COD} \cdot C_F - K_{\mathrm{des}} \cdot C_C) \tag{10}$$

Table 5
Effect of BSPAC addition on the COD removal and microbial growth kinetics

COD (mg/L)	BSPAC (mg/L)	COD removal[a] (%)	μ_{obs} (h^{-1})	$Y_{\text{TSS/COD}}$
2,500	0	70.4	0.0726	0.5664
	4	72.8	0.06114	0.5137
5,000	0	62.4	0.1108	0.9763
	4	69.2	0.0979	0.9011
7,500	0	52.27	0.1421	1.3048
	4	63.73	0.1236	1.0558

[a] COD removal was determined after 24 h.

$$\frac{dC_F}{dt} = -K_{\text{ads}} \cdot \text{COD} \cdot C_F + K_{\text{des}} \cdot C_C \qquad (11)$$

$$\frac{dC_C}{dt} = K_{\text{ads}} \cdot \text{COD} \cdot C_F - K_{\text{des}} \cdot C_C \qquad (12)$$

Eqs. (10)–(12) were solved numerically with MATLAB software (Version 7.12.0.635, 2011) and in particular the solver *ode45,* which is based on the Runge–Kutta formula with an initial guess for the parameters. The particle swarm optimization algorithm, first used by Kenney and Eberhart [28], was selected to optimize and determine the parameters of the Eqs. (10)–(12). A MATLAB program with the general code was written to solve the system of describing differential equations. The three adjustable coefficients ($\alpha, K_{\text{ads}}, K_{\text{des}}$) obtained by performing the program in MATLAB environment are included in Table 6.

The Monod model describes dynamics of micro-organism growth as a function of environmental conditions. The modified Monod equation was used to demonstrate microbial growth and substrate utilization in the biodegradation process. Therefore, the change in microbial growth and substrate concentration based on the complete Monod model is composed by the following coupled differential equations:

$$\frac{d\text{TSS}}{dt} = \mu_{\max} \frac{\text{COD}}{K_S + \text{COD}} \text{TSS} - K_d \cdot \text{TSS} \qquad (13)$$

$$\frac{d\text{COD}}{dt} = -\frac{1}{Y^{T}_{\text{TSS/COD}}} \mu_{\max} \frac{\text{COD}}{K_S + \text{COD}} \text{TSS} \qquad (14)$$

The parameter $\mu_{\max}$ (h^{-1}) *is* the maximum specific growth rate. K_S (mg/L) is called the half-saturation constant or affinity constant, $Y^{T}_{\text{TSS/COD}}$ is described as the true biomass growth yield that is linearly related to the specific rate of biomass growth and the specific

Table 6
Mathematical model parameters (Eqs. (10)–(15))

Process	Initial COD concentration (mg/L)	Parameters						
		α (mg/g)	K_{ads} (L/mg) (h^{-1})	K_{des} (h^{-1})				
Adsorption	6,200	793	9.0593×10^{-4}	0.7287				
		$\mu_{\max}$ (h^{-1})	K_s (mg/L)	K_d (h^{-1})	$Y^{T}_{\text{TSS/COD}}$			
AS	2,500	0.2629	460	0.0562	0.8079			
	5,000	0.5350	541	0.1148	2.3008			
	7,500	0.5479	696	0.1260	2.5098			
		α (mg/g)	K_{ads} (L/mg) (h^{-1})	K_{des} (h^{-1})	$\mu_{\max}$ (h^{-1})	K_s (mg/L)	K_d (h^{-1})	$Y^{T}_{\text{TSS/COD}}$
AS-PAC	2,500	288	8.9387×10^{-5}	0.7348	0.1971	134	0.0301	0.5835
	5,000	521	1.2993×10^{-5}	1.4732	0.4344	274	0.0576	1.9600
	7,500	723	6.3158×10^{-5}	2.6815	0.4723	358	0.0958	2.0480

rate of substrate consumption and K_d (h^{-1}) is the biomass decay constant. Table 6 shows the values obtained for the parameters of the biodegradation at three initial COD concentration levels used in the batch reactor. The parameters were obtained following the same mathematical procedure applied in adsorption study.

To include the effect of PAC addition in the kinetics of biodegradation process, Eq. (14) can be modified as follows:

$$\frac{\mathrm{dCOD}}{\mathrm{d}t} = -\left(\frac{1}{Y^{\mathrm{T}}_{\mathrm{TSS/COD}}}\mu_{\max}\frac{\mathrm{COD}}{K_{\mathrm{S}}+\mathrm{COD}}\mathrm{TSS}\right) - \alpha(K_{\mathrm{ads}}\cdot \mathrm{COD}\cdot C_{\mathrm{F}} - K_{\mathrm{des}}\cdot C_{\mathrm{C}}) \quad (15)$$

Eqs. (13) and (15) were solved numerically following the same mathematical procedure used in the separate adsorption and biodegradation process. The values of model parameters obtained for AS–PAC process are also shown in Table 6.

Table 6 also indicates that the maximum specific adsorption capacity (α) of PAC decreased when PAC was used in AS process. By comparing α values for adsorption and AS–PAC process (at the concentrations of 5,000 and 7,500 mg/L COD), it can be found that the micro-organisms were able to reduce the amount of COD adsorbed on PAC through biodegradation. As a result, renewal of the adsorptive capacity or bioregeneration can occur through the desorption of organic matters by the aids of micro-organisms, which was well addressed by Oh et al. [18]. To demonstrate bioregeneration and desorption of organic matters, Table 6 shows that desorption index (K_{des}) for AS–PAC process (at 5,000 and 7,500 mg/L COD) was more than the value that was obtained for separate adsorption process. During AS–PAC process, at the end of the lag phase, the micro-organisms are responsible for the removal of organic compounds in the bulk fluid [19], thus the COD concentration gradient is created between the PAC surface and bulk liquid and the adsorbed organics are desorbed from PAC; however, the adsorption index (K_{ads}) for AS–PAC process was lower than the adsorption process, due to the blockage of pores by micro-organisms. Furthermore, biofilm developed on the surface of PAC may inhibit the transport of organic matters from liquid to the internal surface of PAC and decrease the adsorption capacity, as was referred by the other researchers worked in this area [26]. The COD concentration gradient between the PAC surface and bulk liquid also affected on adsorption rate. It means that in the AS–PAC process at the lower concentration, i.e. 2,500 mg/L COD, COD concentration gradient surpassed the adsorption of micro-organisms on the PAC surfaces and, hence, the computed K_{ads} value (8.9387×10^{-5} (L/mg) (h^{-1})) was higher than those obtained at higher COD concentrations. In AS–PAC process at 5,000 and 7,500 mg/L COD, both COD concentration gradient and micro-organisms' concentration were at relatively the same high levels. The lowest value for K_{ads} was obtained at the COD concentration of 5,000 mg/L (1.2993×10^{-5} (L/mg) (h^{-1})). It could be attributed to the growth and adsorption of micro-organisms on PAC surface, which prevented adsorption of organic matters. However, in AS–PAC process, at the highest COD concentration of 7,500 mg/L, partial shock loading at initial hours of operation caused the concentration of micro-organisms to remain almost constant. As a result, COD concentration gradient dominated the adsorption of micro-organisms onto the PAC surface and the calculated value of K_{ads} increased to 6.3158×10^{-5} (L/mg) (h^{-1}).

4. Conclusions

In this study, treatment of CWW via adsorption and hybrid biodegradation–adsorption process was investigated. The experimental results indicated an improvement in terms of COD removal by applying hybrid AS–PAC process in lieu of separate AS or adsorption by BSPAC. COD removal efficiency was remarkable at high COD concentration, i.e. 7,500 mg/L, in AS–PAC process, because PAC can reduce the effect of shock loading. One of the concerns about the AS process is the shock loading phenomenon that occurs at high COD load leading to a decrease in COD removal efficiency, while the presence of PAC in AS process could reduce the shock loading effect and the COD removal efficiency remained at high level. The improved removal efficiency achieved at high COD load in the presence of PAC could be a good evidence of its impact on reducing the shock loading phenomenon in AS–PAC process. Therefore, one outcome of the present study was to demonstrate the use of PAC for the treatment of biodegradable wastewaters is not cost-effective at low COD load, while the AS–PAC process could be employed economically at high COD load. A mathematical model was developed to describe the dynamic behavior of the AS, BSPAC adsorption, and AS–PAC process. The model adjustable parameters were recovered by solving the coupled differential equations, following an optimization procedure. The main result of the present study was that the model adjustable parameters could successfully illustrate bioregeneration of BSPAC, decrease of the adsorption capacity, and reduction of the sludge growth in AS–PAC process; however, further investigation is required to develop a more precise mechanism for the combined process.

References

[1] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Organics removal from dairy wastewater by electrochemical treatment and residue disposal, Sep. Purif. Technol. 76 (2010) 198–205.

[2] B.M. Smith, C.C. Ross, J.L. Walsh, Food-processing wastes, Water. Environ. Res. 76 (2004) 1589–1650.

[3] N. Venetsaneas, G. Antonopoulou, K. Stamatelatou, M. Kornaros, G. Lyberatos, Using cheese whey for hydrogen and methane generation in a two-stage continuous process with alternative pH controlling approaches, Bioresour. Technol. 100 (2009) 3713–3717.

[4] R.C. Martins, R.M. Quinta-Ferreira, Final remediation of post-biological treated milk whey wastewater by ozone, Int. J. Chem. React. Eng. 8 (2010). doi: 10.2202/1542-6580.2310.

[5] J. Rivas, A.R. Prazeres, F. Carvalho, F. Beltrán, Treatment of cheese whey wastewater: Combined coagulation−flocculation and aerobic biodegradation, J. Agric. Food. Chem. 58 (2010) 7871–7877.

[6] J. Rivas, A.R. Prazeres, F. Carvalho, Aerobic biodegradation of precoagulated cheese whey wastewater, J. Agric. Food. Chem. 59 (2011) 2511–2517.

[7] F. Carvalho, A.R. Prazeres, J. Rivas, Cheese whey wastewater: Characterization and treatment, Sci. Total Environ. 445 (2013) 385–396.

[8] J.B. Demirel, O. Yenigun, O.O. Onay, Anaerobic treatment of dairy wastewaters: A review, Process. Biochem. 40 (2005) 2583–2595.

[9] J.-C. Frigon, J. Breton, T. Bruneau, R. Moletta, S. Guiot, The treatment of cheese whey wastewater by sequential anaerobic and aerobic steps in a single digester at pilot scale, Bioresour. Technol. 100 (2009) 4156–4163.

[10] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Treatment of dairy wastewater by inorganic coagulants: Parametric and disposal studies, Water. Res. 44 (2010) 5867–5874.

[11] J.P. Kushwaha, V.C. Srivastava, I.D. Mall, Treatment of dairy wastewater by commercial activated carbon and bagasse fly ash: Parametric, kinetic and equilibrium modelling, disposal studies, Bioresour. Technol. 101 (2010) 3474–3483.

[12] S.R. Quasim, W. Chiang, Sanitary landfill leachate: Generation, control and treatment, Technomic, Lancaster, 1994.

[13] A. Ferro Orozco, E. Contreras, N. Zaritzky, Hexavalent chromium removal using aerobic activated sludge batch systems added with powdered activated carbon, Water. SA. 33 (2007) 239–244.

[14] A. Ferro Orozco, E. Contreras, N. Zaritzky, Modelling Cr(VI) removal by a combined carbon-activated sludge system, J. Hazard. Mater. 150 (2008) 46–52.

[15] L.N. Nguyen, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, Removal of trace organic contaminants by a membrane bioreactor–granular activated carbon (MBR–GAC) system, Bioresour. Technol. 113 (2012) 169–173.

[16] N. Lesage, M. Sperandio, C. Cabassud, Study of a hybrid process: Adsorption on activated carbon/membrane bioreactor for the treatment of an industrial wastewater, Chem. Eng. Process. 47 (2008) 303–307.

[17] A. Ferro Orozco, E. Contreras, N. Zaritzky, Dynamic response of combined activated sludge-powdered activated carbon batch systems, Chem. Eng. J. 157 (2010) 331–338.

[18] W.-D. Oh, P.-E. Lim, C.-E. Seng, A.N.A. Sujari, Bioregeneration of granular activated carbon in simultaneous adsorption and biodegradation of chlorophenols, Bioresour. Technol. 102 (2011) 9497–9502.

[19] R.J. de Jonge, A.M. Breure, J.G. van Andel, Bioregeneration of powdered activated carbon (PAC) loaded with aromatic compounds, Water Res. 30 (1996) 875–882.

[20] M. Martin, E. Serra, A. Ros, M. Balaguer, M. Rigola, Carbonaceous adsorbents from sewage sludge and their application in a combined activated sludge-powdered activated carbon (AS-PAC) treatment, Carbon 42 (2004) 1389–1394.

[21] F. Gorzin, A.A. Ghoreyshi, Synthesis of a new low-cost activated carbon from activated sludge for the removal of Cr (VI) from aqueous solution: Equilibrium, kinetics, thermodynamics and desorption studies, Korean J. Chem. Eng. 30 (2013) 1594–1602.

[22] F. Banisheykholeslami, A.A. Ghoreyshi, M. Mohammadi, K. Pirzadeh, Synthesis of a carbon molecular sieve from broom corn stalk via carbon deposition of methane for the selective separation of a CO_2/CH_4 mixture, CLEAN-Soil. Air. Water. (2014). doi:10.1002/clen.201400112.

[23] APHA, Standard methods for the examination of water and wastewater, twenty first ed., American Public Health Association, Washington, DC, 2005.

[24] W. Xing, H.H. Ngo, S.H. Kim, W.S. Guo, P. Hagare, Adsorption and bioadsorption of granular activated carbon (GAC) for dissolved organic carbon (DOC) removal in wastewater, Bioresource. Technol. 99 (2008) 8674–8678.

[25] Q.-S. Liu, T. Zheng, P. Wang, J.-P. Jiang, N. Li, Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, Chem. Eng. J. 157 (2010) 348–356.

[26] T. Widjaja, T. Miyata, Y. Nakano, W. Nishijima, M. Okada, Adsorption capacity of powdered activated carbon for 3,5-dichlorophenol in activated sludge, Chemosphere. 57 (2004) 1219–1224.

[27] Ö. Aktaş, F. Çeçen, Bioregeneration of activated carbon: A review, Int. Biodeter. Biodegr. 59 (2007) 257–272.

[28] J. Kennedy, R. Eberhart, Particle swarm optimization, in: Proceedings of the IEEE International Conference on Neural Network, Perth, Australia, 1995, pp. 1942–1945.