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Fundamentals of mass transfer and kinetics for biosorption of oil and grease from agro-food industrial effluent by *Serratia marcescens* SA30

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Abstract

Fundamental studies of mass transfer and kinetics are essential for a detailed understanding of the characteristics and the mechanisms of biosorptions. In this study, the modified mass transfer factor models were used to assess the rates of global, external and internal mass transfer for the biosorption of oil and grease (O&G) from agro-food industrial effluent (AFIE) by *Serratia marcescens* SA30. Using a packed-bed column reactor to run the experiments at different O&G concentrations, this study finds that the global mass transfer rate increases exponentially accompanied with the sudden increase of the cell surface sorption. The influence of concentration on the external mass transfer is very remarkable due to the effects of driving force and biomass growth can lead to a rapid movement of O&G molecules from the bulk water to extracellular precipitation. The resistance to mass transfer could be dependent on intracellular accumulation at the beginning and then on film mass transfer at the final stage of biosorption of O&G by *Serratia marcescens* SA30. This study would provide a green and sustainable pathway for removing O&G from AFIE.

Keywords: Agro-food industrial effluent; Biosorption; Mass transfer kinetics; Oil and grease; Packed-bed column reactor; *Serratia marcescens* SA30.

1. Introduction

Oil and grease (O&G) spilled into rivers and lakes pose a major threat to aquatic environments, killing or adversely affecting fish and other aquatic organisms. Sensitivity of aquatic organisms to O&G toxicities would be associated with the tendency to block oxygen entering water from the atmosphere, due to O&G, which has a lower specific gravity than water, floats on top of water. It is evident that waste cooking oil, animal fats, yellow grease, brown grease and waste from vegetable oil refining industries are the major sources of waste oil for O&G production. Vegetable oils are well known for their liquid, oily and fatty texture; therefore, the use of vegetable oils can have to fulfill two roles: they can either be used for cooking oil or

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for fuel and diesel production. The global production of vegetable oils has seen a steady increase since the beginning of the century,[1-3] reaching a peak of 170.01 million metric tons in 2013/2014. Spilled O&G tends to accumulate in the environment, causing soil and water pollution. Used O&G that is incidentally captured by a wastewater treatment system as part of routine process operations at a food service facility is exempt from the requirement of the specific pretreatment standards. For example, approximately 9000 restaurants and more than 200 fast-food shops in Hong Kong use over half a million tons of water everyday and release their oil-contaminated wastewater into the municipal wastewater collection and treatment works. Due to O&G decomposes very slowly, it reduces the oxygen supply to the microorganisms that break more complex organic molecules of O&G into simpler substances. The O&G contained in the wastewater can aggregate and fouls the sewer system and generates an unpleasant odour.[4] A number of countries have implemented more stringent regulatory standards for O&G, such that: (1) the United States Environmental Protection Agency (USEPA) sets the daily maximum limit at 42 mg L^{-1} and the monthly average limit at 29 mg L^{-1} for O&G, (2) the Convention for the Protection of Marine Environment of the North-East Atlantic sets the annual average limit for discharge O&G into the sea at 40 mg L^{-1}, (3) the permitted offshore discharge of O&G in produced water in Australia is 30 mg L^{-1} and (4) the monthly average limit for O&G in China is 10 mg L^{-1}.[5-6]

Some conventional physical and chemical treatments such as filtration, coagulation, adsorption and advanced oxidation process have been proposed to remove O&G from a contaminated water. Application of these removal methods depends on the end usage of treated water and the amount of O&G presented in the contaminated water. The treatment of oily wastewater produced from post-treatment unit of the refinery processes using flocculation and micro-filtration with zirconia membrane can meet the stringent regulatory standards.[7] Combined use of aluminum and iron as electrode materials in the electrocoagulation unit can yield a high process performance for the removals of chemical oxygen demand (COD) and O&G with respect to the stringent effluent standards.[8] The removal of O&G from oily automotive wastewater by adsorption after chemical de-emulsification may show a trend similar to that of COD.[9] The advanced oxidation processes can be very profitably employed for the removal of mineral oil pollutants in wastewaters.[10] Once the release of O&G into the environment occurred, choice of the removal methods should have a significant impact on the final reported O&G removal efficiency. The use of physical and chemical treatment processes requires high capital and operating cost; along with the wastes, by-products generated may be difficult to monitor and control.[11] In recent years, biosorption developed into a promising alternative method for environmental remediation and has proved to be very effective in the removal of inorganic and organic pollutants from aqueous solution.[12-17] However, the fundamentals of mass transfer and kinetics for biosorption of O&G from wastewater by bacterial degradation process have not been fully understood. The aims of this study are to identify the intrinsic kinetics, to assess the influence of external and internal mass transfer and to determine the resistance of mass transfer for the biosorption of O&G from an agro-food industrial effluent (AFIE), attached onto the oil palm frond (OPF).

2. Materials and Methods

2.1. Agro-food industrial effluent

The samples of agro-food industrial effluent (AFIE) were collected from an agro-food factory located at Batu Pahat, Johor, Malaysia. The samples being transported to testing laboratory for the purpose of this research were filled in a 1-L sterilised Schott bottle and then must be maintained at an appropriate temperature and kept in an ice-packed container. The main characteristics of the AFIE are depicted in Table 1 to show that such an agro-food factory may generate an effluent highly contaminated with O&G; therefore, this study used the AFIE sampes to assess the ability of the biosurfactant-producing bacteria to remove O&G by a biosorption process. Table 1 shows the criteria used to determine whether a measure of the AFIE parameters has been considered for the purpose of O&G removal by a biological treatment process. Since the amount of COD is lower compared to that of O&G then the organic matters present in AFIE sample can be visualised as oxidizable and non-oxidizable organic compounds, the presence of both NH_4^+ and TDS at a sufficient enough concentration can be suggested as the essential elements required for bacterial growth.[18] Therefore, it is expected that the use of locally isolated biosurfactant-producing bacteria can enhance the O&G removal of the AFIE in a hydrodynamic column.

Table 1 Main characteristics of the AFIE

No	Parameter	Unit	Range in the concentrations	Analytical method
1	COD	mg O_2 L^{-1}	9500 -33000	Dichromate digestion
2	NH_4^+	mg N L^{-1}	0 - 309.9	Polarographic sensor (YSI Model 5100)
3	SS	mg L^{-1}	625 - 6000	Gravimetric
4	TDS	mg L^{-1}	738 - 1518	Polarographic sensor (YSI Model 5100)
5	O&G	mg L^{-1}	23938 -128007	Partition Gravimetric

2.2. Isolation, growth condition and identification of the bacteria

A 2.5-mL sample of the AFIE was transferred from the Schott bottle to a 22.5 mL of nutrient broth (NB) medium in a 250-mL Erlenmeyer flask as active culture and made to order with three active cultures. Each live active culture was then shaken at 25, 30 and 37^{o}C with constant rotation (200 rpm). After the incubation periods of 24 and 48 hours, a loop of each incubated active culture was inoculated by streaked plate technique onto a sterilised nutrient agar (NA) plate and then incubated again at 25, 30 and 37^{o}C for selecting the isolation of a single colony. A few hundred bacterial colonies isolated from the AFIE were examined based on the same morphological features i.e. form, margin, surface, elevation, colour, opacity and gram staining to reduce such bacterial colonies to ten single colonies, according to the Bergey's Manual of Determinative Bacteriology.[19] The typical colony was carefully selected streaked again onto a sterilised NA plate and incubated at 25, 30 and 37^{o}C for obtaining a pure culture. In general, the cultures grown effectively at 30°C should never be kept for more than 15 days. Ten single colonies that originally coming from oil-contaminated wastewater of agro-food industry were then successfully isolated from the NA medium, and the live active cultures were kept in a Luria Bertani (LB)-glycerol medium for the further uses. Then the only one strain identified as *Serratia marcescens* SA30 has shown an optimal OD_{600} of greater 1.0 to be feasibly selected it for potential use in the experiments with a packed-bed column reactor (PBCR).

2.3. Bacteria and bacterial acclimatization

This study used the *Serratia marcescens* SA30 strains for performing the biosorption of O&G from AFIE run in a PBCR that filled with OPF. The choice of OPF as the holding media required for biomass growth was based on abundantly available and cheap materials. The strains of *Serratia marcescens* SA30 as biosurfactant-producing bacteria, which having its submitted sequence appears in the GenBank nucleotide sequences databases under accession number KF686740, were identified using the basic local alignment search tool (BLAST) carried out by the Vivantis Technologies Sdn Bhd Laboratory, Selangor, Malaysia. An experiment involving in vitro rooting and acclimatisation in the PBCR treatment system was performed with the use of *Serratia marcescens* SA30 strains during a period of 15 days, with the addition of NB. The decrease in NB concentration within the PBCR must be gradually balanced by an increase in the O&G concentration in AFIE. After 15 days, the NB solution was totally replaced with AFIE solution, which contains high concentration of O&G.

2.4. Packed-bed column reactor and experimental procedure

For the purpose of this study, the PBCR (see Fig. 1) consisting of acrylic column with its dimensions of 50.0-cm height × 4.6-cm inner diameter, AFIE storage tank with a capacity of 5 L, Masterflex peristaltic pump (Cole-Palmer) and treated AFIE storage tank with a capacity of 3 L was used to conduct the experiment. An acrylic column was used as a packed-bed column, vertically dividing into four different sections from bottom to top where 2-cm height filled with an inert stone of 1 to 2-cm granular size, 35-cm height filled with a dried OPF of 90 g, 3-cm height filled with an inert stone of the same granular size and 10-cm empty column height. The inert stones require to be soaked in a pure water for 24 hours in order to remove the impurities, rinsed with distilled water and dried at 30^{o}C in an incubator of Memmert IN110 for 24 hours. The packed-bed column filled with OPF of 1 to 2-cm length range was used as the supporting materials for baterial cell immobilisation during the AFIE treatment. The volume (empty space) of the active zone of being filled with the OPF was 0.46 L. The OPF was rinsed with 2-L deionised water at a constant flow rate of 0.18 L h^{-1} to prevent potential clogging of the PBCR and to allow electrostatic charge and hydrophobic interactions necessary for bacterial adhesion to the supporting materials. The *Serratia marcescens* SA30 strains were immobilised on the OPF surface with the help of a Masterflex peristaltic pump (Cole-Palmer) with continuous circulation at the same flow rate as the rinsing step to allow initial bacterial attachment for 3 days until the PBCR treatment system reaches steady state conditions.[20-21] The purpose of using an empty column of 10 cm on the top to ensure the consistent availability of the oxygen supply was to allow growth of the *Serratia marcescens* SA30 to be immobilised and securely held on the surface of OPF. Because when the air present in the empty column of the PBCR and the water of the AFIE meet, this tremendous difference in concentration can cause oxygen molecules in the air to dissolve into the water. The effects of different initial O&G concentration (i.e. 16424, 26072 and 33548 mg L^{-1}) on the biosorption of O&G processed by *Serratia marcescens* SA30 were aimed premarily at understanding the behaviours of global, external and internal mass transfer. The samples collection was carried out for each experiment during 6 days.

2.5. Numerical simulation

The total O&G quantity accumulated in the biomass-attached OPF of the packed-bed column for a given feed concentration and flow rate can be calculated by the following formula:[22]

$$q = \int_0^V \frac{(C_o - C_s)dV}{m} \quad (1)$$

where, q is cumulative quantity of the O&G to accumulate into the biomass attached the OPF (mg g^{-1}), C_o is concentration of the O&G to entry into the column (mg L^{-1}), C_s is the concentration of the O&G to depart from the column (mg L^{-1}), V is effective volume of the treated water (L) and m is amount of the OPF in the column (g).

This study used the modified mass transfer factor (MTF) models developed by Fulazzaky et al.[23] for modelling the mass transfer zone behaviours of O&G bioaccumulation by *Serratia marcescens* SA30 because of such kinetic models are applicable for assessing competitive effect of the biosorption of multifarious solute from contaminated waters. The use of the following equation[23-24] would be able to describe the mass transfer process during the biosorption of O&G onto OPF from AFIE, such that:

$$\ln\left(\frac{C_o}{C_s}\right) = [k_L a]_g \times e^{-\beta \times \ln(q)} \times t \quad (2)$$

where $[k_L a]_g$ is global mass transfer factor relating to the actual rate of global mass transfer (h^{-1}), β is adsorbate-adsorbent affinity parameter (g h mg^{-1}), and t is accumulation time (h).

A mathematical deduction of eqn (2) does give us the linear equation of:

$$\ln(q) = \frac{1}{\beta} \times \ln(t) + B \quad (3)$$

with

$$B = \frac{\ln([k_L a]_g) - \ln\left\{\ln\left(\frac{C_o}{C_s}\right)\right\}}{\beta} \quad (4)$$

where B is potential mass transfer index relating to driving force of mass transfer (mg g^{-1}).

To having the values of $[k_L a]_g$ at the desired C_0/C_s ratios can be calculated using eqn (4) since the index B and the parameter β have been verified from the linear curve of plotting $\ln(q)$ versus $\ln(t)$, and then a curve of plotting $[k_L a]_g$ versus C_s/C_0 can be proposed to get an insight on global mass transfer (GMT) for the biosorption of O&G from AFIE by *Serratia marcescens* SA30. The mathematical equation to express the relation[21] of external to global mass transfer is as follows:

$$[k_{\mathrm{L}}a]_{\mathrm{f}} = [k_{\mathrm{L}}a]_{\mathrm{g}} \times e^{-\beta \times \ln(q)} \quad (5)$$

where $[k_{\mathrm{L}}a]_{\mathrm{f}}$ is external mass transfer factor or film mass transfer factor or volumetric film mass transfer coefficient relating to the actual rate of external mass transfer (h^{-1}).

For this numerical simulation, to having the values of q in eqn (5) at the desired C_s/C_0 ratios should use interpolation and extrapolation. Then using eqn (5) permits us to compute the values for variable $[k_{\mathrm{L}}a]_{\mathrm{f}}$ based on the values of q obtained from interpolation and extrapolation since the parameter β has been verified from slope on a straight line of plotting $\ln(q)$ versus $\ln(t)$ in eqn (3) and the values for variable $[k_{\mathrm{L}}a]_{\mathrm{g}}$ in accordance with the desired C_s/C_0 ratio have been computed using eqn (4). Internal mass transfer factor is recognised as the difference between global and film mass transfer factor and can be written as follows:[23, 25]

$$[k_{\mathrm{L}}a]_{\mathrm{d}} = [k_{\mathrm{L}}a]_{\mathrm{g}} - [k_{\mathrm{L}}a]_{\mathrm{f}} \quad (6)$$

where $[k_{\mathrm{L}}a]_{\mathrm{d}}$ is internal mass transfer factor relating to the actual rate of internal mass transfer (h^{-1}).

Using eqn (6) permits us to compute the values for variable $[k_{\mathrm{L}}a]_{\mathrm{d}}$ in accordance with the C_s/C_0 ratio since the values for both variables $[k_{\mathrm{L}}a]_{\mathrm{g}}$ and $[k_{\mathrm{L}}a]_{\mathrm{f}}$ have been verified.

3. Results and Discussion

3.1. Linear regression analysis

A plot (Fig. 2) of $\ln(q)$ versus $\ln(t)$ should yield a straight line with a slope of β^{-1} and an intercept of B. Empirical evidence indicates that correlation for all parameters in eqn (3) is very good ($R^2 > 0.93$; see Table 2), meaning that the parameters B and β can be used to describe the kinetic mechanisms of bioaccumulation of O&G assimilation by *Serratia marcescens* SA30 from AFIE, attached on the surface of OPF. It is well recognised that biosorption of solute from aqueous solution can be classified according to the location, i.e.: (1) extracellular accumulation/precipitation, (2) cell surface sorption/precipitation and (3) intracellular accumulation.[26-27] Experimental evidence suggests the variability in C_0 value governing the growth and metabolism of *Serratia marcescens* SA30 due to driving force for the transport of O&G from bulk water to film zone (extracellular accumulation) would increase with increasing of O&G concentration. This would have the effects of increasing the value of β from 1.663 to 2.064 and to 2.609 g h mg^{-1} and that of B from 3.378 to 4.371 and to 5.550 mg g^{-1} with increasing of C_0 value from 16424 to 26072 and to 33548 mg L^{-1}, respectively (see Table 2). Biosorption mechanisms of O&G from aqueous solution to active chemical groups on the cell wall matrix of *Serratia marcescens* SA30 and then following by intracellular accumulation may consist of various interactions of such as physical adsorption, chemical binding of ionic groups and ion exchange,[28] and they are still not very well understood and thus must be verified by the analysis of global, external and internal mass transfer.[23, 25] Cell walls of microbial biomass mainly composed of polysaccharides, proteins and lipids offer abundant functional groups such as carboxyl, hydroxyl, phosphate and amino acids, as well as hydrophobic

adsorption sites such as aliphatic carbon chains and aromatic rings.[29] It is suggested that cell surface sorption is a physicochemical interaction, which is not dependent on bacterial metabolism. Such a phenomenon is hardly dependent on the interaction of the available molecules on the cell walls and can be reversible.[30]

Table 2 Values of β and B for different values of C_0, obtained from slope and interception, respectively, of plotting ln(q) versus ln(t)

C_0 (mg L^{-1})	β (g h mg^{-1})	B (mg g^{-1})	R^2
16424	1.663	3.378	0.9886
26072	2.064	4.371	0.9349
33548	2.609	5.550	0.9640

The FTIR test (see Fig. 3) of the OPF sample verified that the surface functional groups were found as: -OH at the IR absorption band of 3358 cm^{-1}, C-H at 2917 and 2894 cm^{-1}, C=O at 1733 cm^{-1}, C=C at 1638 cm^{-1}, $-CH_2$ at 1463 and 1416 cm^{-1}, $-CH_3$ at 1377 cm^{-1}, C-O at 1059 and 1033 cm^{-1} and C-Cl at 798 and 719 cm^{-1}.[31-34] Additional evidence for the existence of such active sites leading to the safe and correct immobilisation of *Serratia marcescens* SA30 (microbial biomass) on the surface of OPF during the experiment could be due to the microbial biomass consisting of small particles with low density, poor mechanical strength and little regidity can encourage interaction in many ways based on a set of chemical and physical mechanisms.[35] The OPF of using the low cost locally available materials[36] shows favorable activity and attractability on the biosorption of O&G and can be used for long times with progressively increase the removal performance.[37]

3.2. Kinetic and global mass transfer

In this study, an attemp of plotting $[k_La]_g$ versus C_s/C_0 (see Fig. 4) has made to yielding the logarithmic equation: $[k_La]_g = \alpha \times \ln(C_s/C_o) + \gamma$, where α is the GMT rate coefficient relating to microbial growth kinetics (in h^{-1}) and γ is the biomass yield rate constant relating to substrate in the solution (in h^{-1}). Correlation for the parameters α and γ is excellent ($R^2 = 1.00$; see Table 3). This would be very useful to use the parameters α and γ as indicator for assessing the GMT phenomena in biosorption of O&G assimilation by *Serratia marcescens* SA30 from an AFIE. A logarithmic increase (see Figs. 4a, b, c) was verified for all $[k_La]_g$ trends of different values of C_0 since the expected trends for bacterial growth of feeding the fixed C_0 value to such a biological treatment system increase logarithmically in the number of *Serratia marcescens* SA30 bacteria in the PBCR. After achieving 100% removal efficiency, the values of γ as high as 1265, 80397 and 8943510 h^{-1} were verified for the PBCR treatment system feeding with the C_0 values of 16424, 26072 and 33548 mg L^{-1}, respectively, meaning that the increases in C_0 value of 9648 and 17124 mg L^{-1} in PBCR may increase the values of γ as high as 63.5 and 7069 times, respectively. This study verified that on doubling the C_o value, the potential rate of biomass yield might increase by approximately 111 times. This would be suggested that the GMT rate increases exponentially accompanied with the sudden increase of the cell surface sorption and hence the increased driving force in diffusion of O&G from the bulk water to extracellular accumulation could be reasonable. In addition, rapid, exponential growth and increased biomass yield of *Serratia marcescens* SA30 strains can attract large quantities of O&G from AFIE hence the GMT increase exponentially.[38]

Table 3 Values of α and γ for different values of C_0, obtained from logarithmic slope and biomass yield rate constant, respectively, of plotting $[k_La]_g$ versus $\ln(C_s/C_o)$

C_0 (mg L^{-1})	α (h^{-1})	γ (h^{-1})	R^2
16424	274.7	1265	1.0000
26072	17456	80397	1.0000
33548	2×10^6	8943510	1.0000

3.3. Kinetic and external mass transfer

The use of the MTF models developed by Fulazzaky[25] was able to describe the phenomena of external and internal mass transfer for the adsorption of different surfactants as a single solute and then confirmed it applicable for the adsorption of another single solutes i.e. atrazine and simazine[39] from aqueous solution onto porous material (i.e. granular activated carbon) applied to a hydrodynamic column. Such the theoretical adsorption models were then empirically modified by Fulazzaky et al.[23] and then confirmed again applicable for assessing competitive effect[40] of the adsorption of multifarious solute from contaminated waters onto porous material.[24] The purpose of this study was to use the modified MTF models[23] to assess the biosorption behaviours of O&G by *Serratia marcescens* SA30 immobilised in PBCR, aiming at a good understanding of wide applicability of the models, and thus provides valuable insights into the dynamic behaviour of biological process. The significance of the biomass yield of the biosorption to affect the EMT rate can be analysed when the different values of C_0 were used for the experiments, because the attractive force between the solute and the biomass relates to driving forces. Considering that the potential growth rate of *Serratia marcescens* SA30 for higher C_0 level is faster than for a lower one, it seems that the influence of C_0 on the EMT is very remarkable, due to the effects of driving force and biomass growth this can lead to a rapid movement of O&G molecules from the bulk water to extracellular precipitation. Experimental data verification (Figs. 5a, b, c) showed that, at 5% of the C_s/C_o ratio, the maximum $[k_La]_f$ value of 962338×10^6 h^{-1} for the biosorption of O&G by *Serratia marcescens* SA30 in PBCR treatment system feeding with C_0 = 33548 mg L^{-1} (see Fig. 5c) is very far higher than both the maximum $[k_La]_f$ values of 4187808 h^{-1} for that feeding with C_0 = 26072 mg L^{-1} (see Fig. 5b) and 2735 h^{-1} for that feeding with C_0 = 16424 mg L^{-1} (see Fig. 5a). The transport of O&G molecules from the bulk water to reaching the extracellular precipitation is very fast when the biosorption process involves a high concentration gradient. The effect of EMT on growth and biomass yield may reduce the thickness of the cell membrane[41] and leads to increased cell surface sorption. The results (Figs. 5a, b, c) show that the variations of $[k_La]_f$ rapidly decrease when the C_s/C_o ratio should be less than 20%, even though the EMT increases at the beginning until the C_s/C_o ratio reaches at 5%. This can be described by extracellular accumulation of O&G molecules fused to the cell surface sorption, because the increased O&G concentration in film zone can reduce the driving force[23, 25] to control the movement of the O&G molecules from the bulk water to extracellular precipitation. The transport of O&G molecules from the extracellular precipitation to cell surface sorption and then following by intracellular accumulation may consist of various physicochemical interactions and thus must be verified by the analysis of internal mass transfer (IMT).

3.4. Kinetic and internal mass transfer

The results (Figs. 4, 5) of the numerical simulation show that the increase in C_0 value from 16424 to 26072 to 33548 mg L^{-1} can greatly increase the values of $[k_La]_g$, $[k_La]_f$ and $[k_La]_d$. This would be due to the multiplication rate of exponential growth of *Serratia marcescens* SA30 can produce a large amount of the biosurfactant that reduces the interfacial surface tension between oil and water[42] to having a great effect on the actual rates of global, external and internal mass transfer when the concentration of O&G in AFIE as the sources of carbon and energy for such biosurfactant-producing bacteria increases. Due to *Serratia marcescens* SA30 strains accumulated O&G intracellularly (see Fig. 6; thick arrow-1) during growth on the surface of OPF can produce potentially interfering metabolites (biosurfactants) that regulate cell growth and metabolism in response to environmental cues, this biological phenomenon does contribute to differ IMT for different values of C_0 feeding the PBCR traetment system. Mass transfer equations have been developed to model the circumstances of IMT. The use of eqn (6) permits us to determine the variations of $[k_La]_d$ pursuant to the C_s/C_o ratio if the variations of $[k_La]_g$ and $[k_La]_f$ have been verified using the eqn (4) and eqn (5), respectively. The results (Figs. 5a, b, c) show that all the $[k_La]_d$ curves by exception before reaching at 5% of the C_s/C_o ratio have an increasing trend from the negative value to finally reach at a positive value after 18% of the C_s/C_o ratio for the PBCR treatment system feeding with C_0 = 16424 mg L^{-1} (see Fig. 5a), after 47% of the C_s/C_o ratio for that feeding with C_0 = 26072 mg L^{-1} (see Fig. 5b) and after 75% of the C_s/C_o ratio for that feeding with C_0 = 33548 mg L^{-1} (see Fig. 5c). However these $[k_La]_d$ curve raising trends of the IMT are continually counterbalanced by the EMT decreasing processes that decrease the $[k_La]_f$ curves (see Figs. 5a, b, c) yielding the continuous logarithmic increase of the $[k_La]_g$ curve starting from zero until the last point when the GMT has its optimal value at 100% of the C_s/C_o ratio (see Figs. 4a, b, c). The resistance of mass transfer for the biosorption of O&G by *Serratia marcescens* SA30 could be dependent on the intracellular accumulation before and the film mass transfer after reaching the C_s/C_o ratios of 18, 47 and 75% for the PBCR treatment system feeding with the C_o values of 16424, 26072 and 33548 mg L^{-1}, respectively. Although it is well known that *Serratia marcescens* SA30 bacteria develop reducing large amounts of O&G in the AFIE during growth,[43] the lowest potentials being generated during the logarithmic phase of growth can have dramatic effects on the IMT factor. In this study, the increases in $[k_La]_d$ value were verified as high as 3006, 3127675 and 951312929608 h^{-1} for the PBCR treatment system feeding with C_0 = 16424 mg L^{-1} (see Fig. 5a), for that feeding with C_0 = 26072 mg L^{-1} (see Fig. 5b) and for that feeding with C_0 = 33548 mg L^{-1} (see Fig. 5c), respectively. However, the transport of O&G molecules from the extracellular precipitation to the cell surface sorption could be difficult at the early stages of IMT as this crosslinks the triglycerides consisting of three molecules of fatty acid combined with a molecule of the alcohol glycerol into a network of tough (fibrous molecules), which is responsible for the mechanical strength of bacterial cell walls.[44] The rate-limiting step in O&G accumulation depends on the IMT resistance, as the EMT resistance and kinetic limitations would make negligible on rolling resistance.[45] Thus the *Serratia marcescens* SA30 bacteria cannot reproduce as proficiently as during the adaptation phase, and then the ability of bacterial metabolism and growth increases to accommodate the transport of high amounts of O&G fused into the cell surface when most of the triglycerides entering the cell is fixed into organic carbon. Once entering the cell, more complex organic molecules of the O&G begin to break down into simpler substances by catabolic reactions. The

simpler substances can be combined by anabolic reactions to form more complex organic molecules of the biomass hence the biomass yield increases. Anabolic reactions in bacteria require energy and therefore the energy of catabolic reactions can be used to drive anabolic reactions. Significant amount of the organic carbon may accumulate as intracellular granules (see Fig. 6; thick arrow-2) by *Serratia marcescens* SA30 strains as they enter the stationary phase of growth, to be used later as an internal reserve of carbon and energy.

4. Conclusions

This study used the modified MTF models to scrutinise the biosorption behaviours and mechanisms of O&G assimilated by *Serratia marcescens S*A30 from AFIE. The efforts made can provide new insights concerning various C_o levels of conducting a hydrodynamic modelling study of the PBCR to determine the global, external and internal mass transfer. Rate of EMT should be proportional to the driving force being a concentration gradient between the bulk water phase and the film zone associated with the extracellular precipitation. Rate of IMT in the biosorption of O&G by *Serratia marcescens S*A30 strains could be proportional to the growth and biomass yield and depends on the available biomass. This study justified that the rate-limiting step in O&G accumulation depends on the IMT resistance, as the EMT resistance and kinetic limitations would make negligible effect on rolling resistance.

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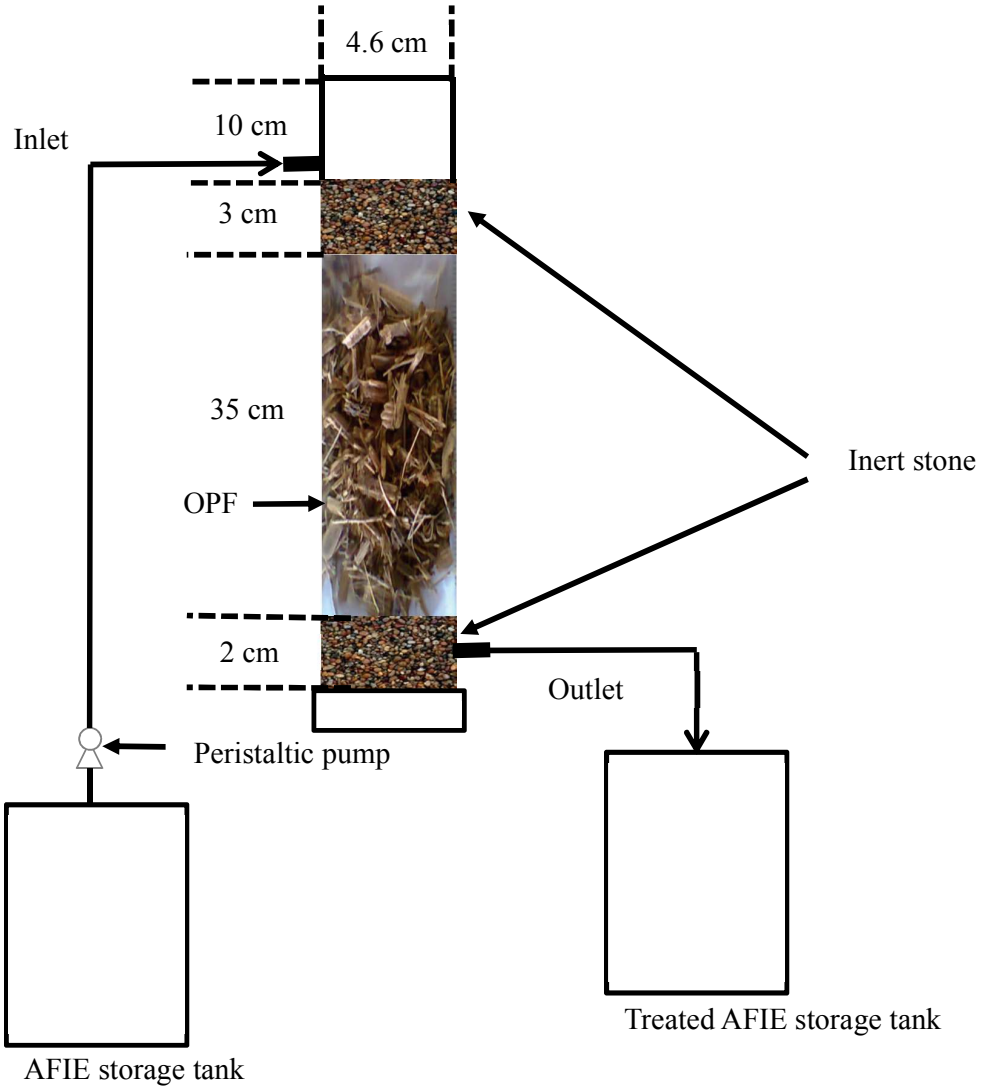


Figure 1 Schematic of the PBCR

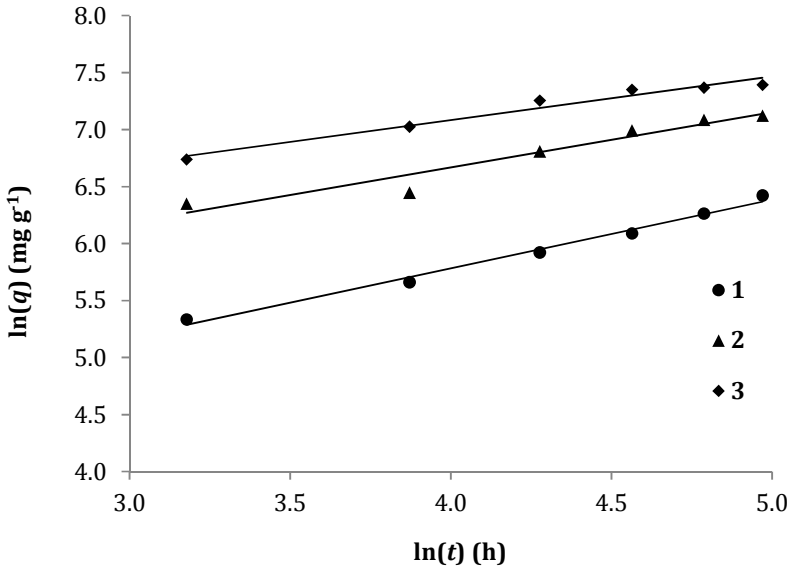


Figure 2 Curves of plotting ln(q) versus ln(t), with **(1)** C_0 = 16424 mg L^{-1}, **(2)** C_0 = 26072 mg L^{-1} and **(3)** C_0 = 33548 mg L^{-1}

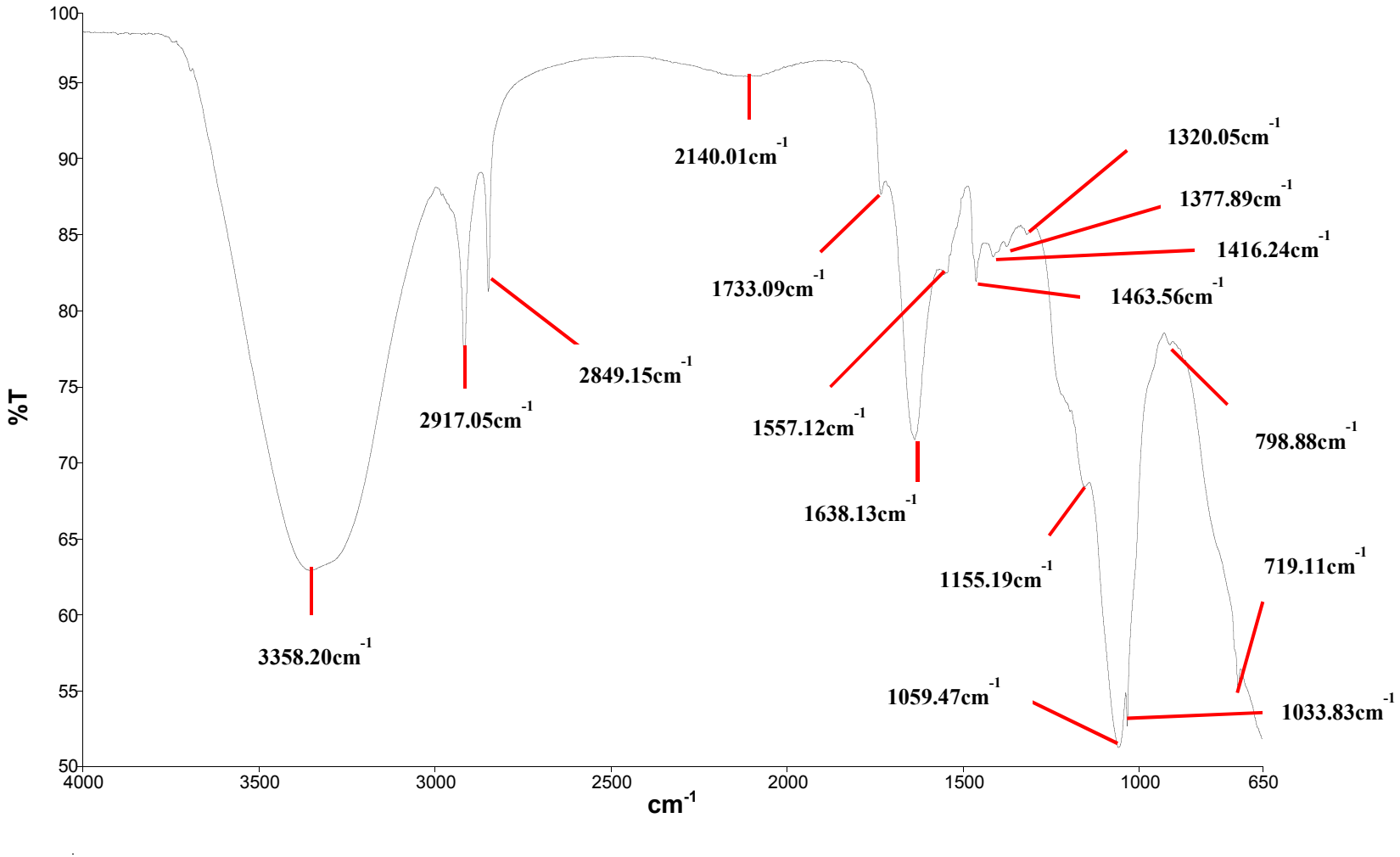
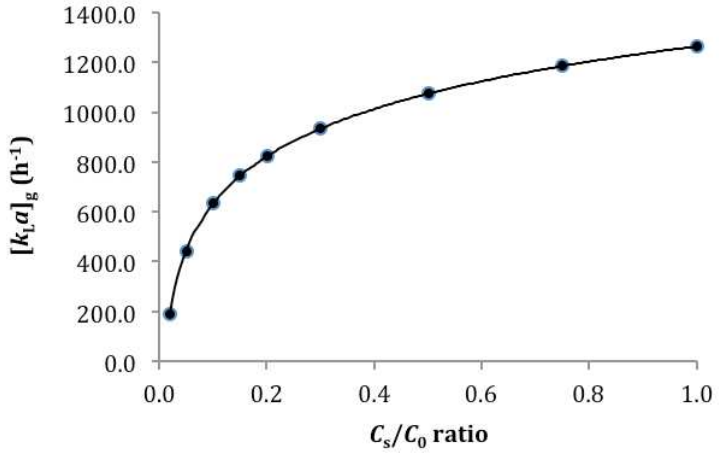


Figure 3 FTIR spectra of the OPF sample

(a)



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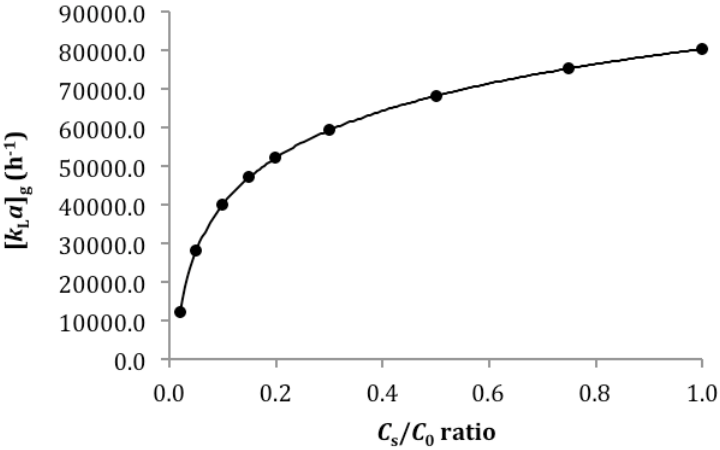


(c)

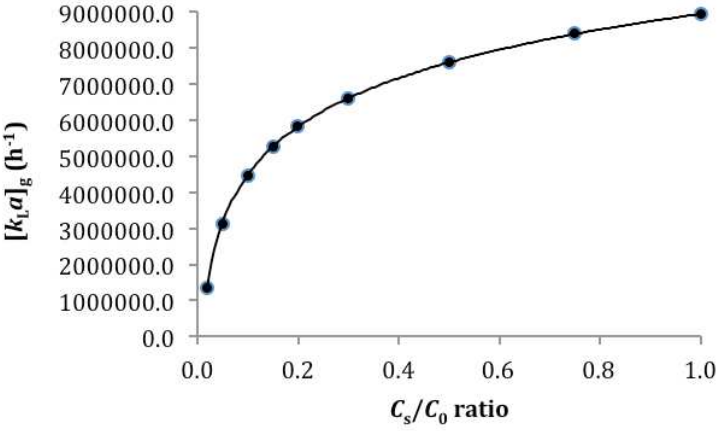
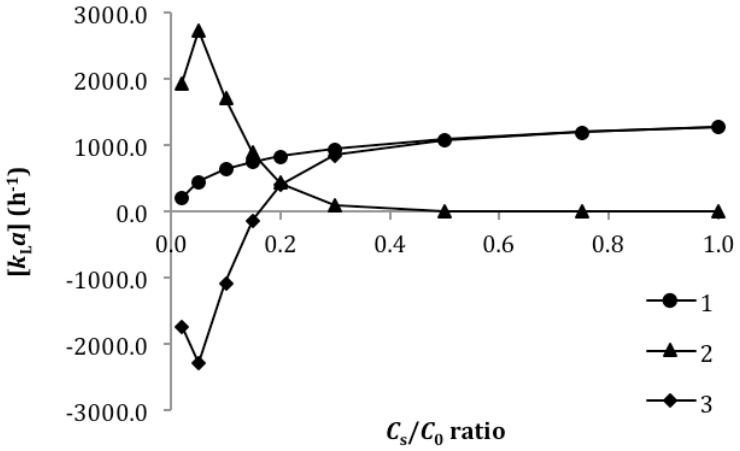


Figure 4 Curves of plotting $[k_L a]_g$ versus C_s/C_o ratio, with **(a)** C_0 = 16424 mg L^{-1}, **(b)** C_0 = 26072 mg L^{-1} and **(c)** C_0 = 33548 mg L^{-1}

(a)



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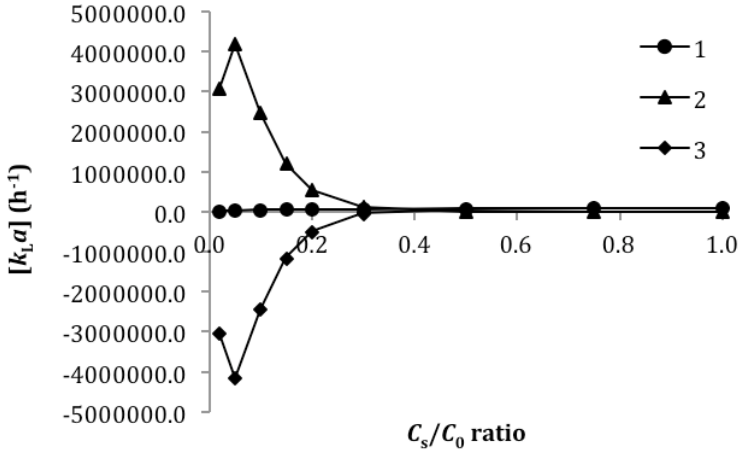

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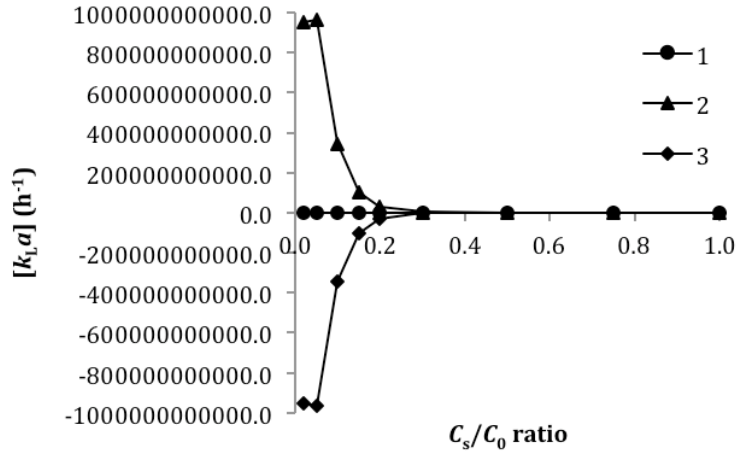

Figure 5 Curves of plotting (1) $[k_L a]_g$, (2) $[k_L a]_f$ and (3) $[k_L a]_d$ against C_s/C_o ratio, with **(a)** C_0 = 16424 mg L^{-1}, **(b)** C_0 = 26072 mg L^{-1} and **(c)** C_0 = 33548 mg L^{-1}

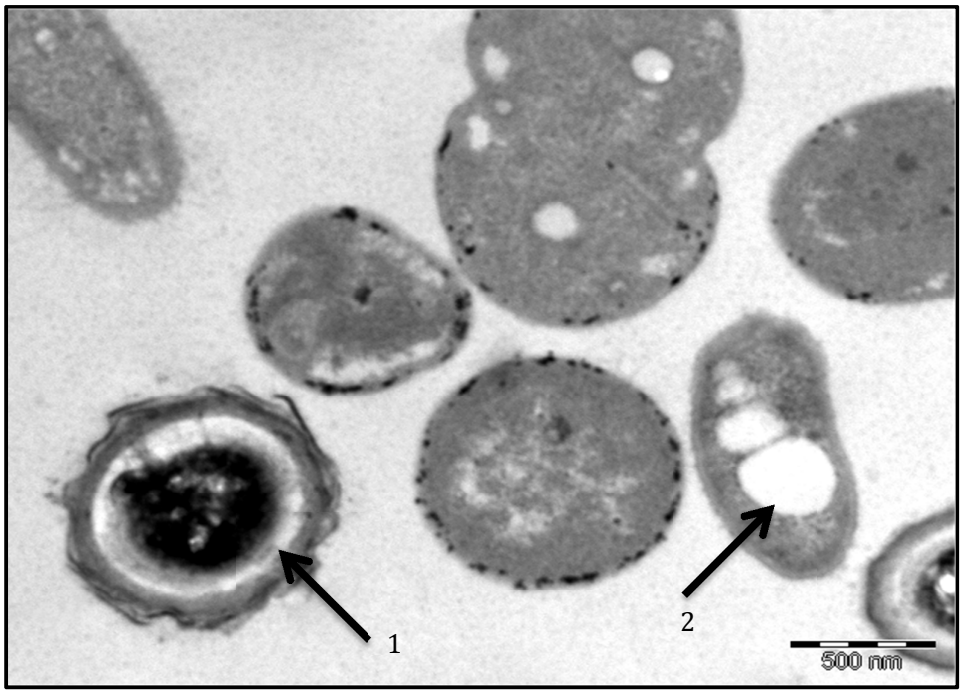

Figure 6 TEM image of *Serratia marcescens* SA30 to show that an intracellular accumulation of O&G exists within cell membrane

Biosorption mechanisms of oil and grease removal by *Serratia marcescens S*A30 from agro-food industrial effluent, attached on the oil palm frond