original article

A comparative study between dried anaerobic digested sludge and dried activated sludge for the removal of 4-chlorophenol from aqueous solutions

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ABSTRACT

Aims: In this study, the adsorption capacity of dried anaerobic digested sludge (DADS) and dried activated sludge (DAS) for the removal of 4-chlorophenol (4-CP) from aqueous solutions was evaluated.

Materials and Methods: Both anaerobic digested sludge and activated sludge were collected from a south municipal wastewater treatment plant in Isfahan. Batch biosorption experiments were carried out to investigate the effects of solution pH, contact time, biosorbent dosage and initial concentration of 4-CP. The residual concentration of 4-CP was analyzed by colorimetry method. Isotherms and kinetic equations were applied to study kinetic and equilibrium of adsorption.

Results: Results indicated that, DAS have higher removal potential in comparison with DADS. The optimum pH was detected to be 3 for DADS and 4 for DAS. By increasing contact time and biosorbent dosage, removal efficiency of 4-CP increased for both biosorbents. Furthermore, a decreasing trend was observed when initial concentrations were increased. The equilibrium time for DAS was 2.5 h and for DADS was 4 h. The maximum adsorption capacity were found 1.67 mg/g for DAS and 0.93 mg/g for DADS. The 4-CP removal equilibrium isotherm was modeled by Freundlich equation. Kinetic studies suggested that pseudo-first-order model for DADS and second order for DAS were the best choices to describe biosorption behavior.

Conclusion: According to the present study, DAS, have better efficiency for the removal of 4-CP in comparisons with DADS.

Key words: 4-chlorophenol, activated sludge, biosorption, digested sludge

INTRODUCTION

Chlorophenol compounds and their derivatives are considered priority pollutants in the environment.[1] The major health effects with exposure to high levels of phenolic compounds are headache, loss of appetite, rapid fatigue and sever chronic insomnia.[2] These compounds are used as intermediates for manufacturing agricultural chemicals, pharmaceutical, and dyes. Chlorophenols get into the body

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of water from a variety of sources such as industrial waste, pesticide, and insecticides.[3,4] The phenolic compound may also be produced during disinfection of water and wastewater with chloride in the present of certain contaminants.[5] Activated carbon adsorption, chemical oxidation, aerobic/anaerobic biological degradation, coagulation, solvent extraction and liquid membrane permeation are existing methods for remediation of chlorinated aromatics, but they are expensive and ineffective.[1,6] The adsorption onto activated carbon is widely used to remove phenolic compounds from the wastewater. The high cost of activated carbon has stimulated the interest of researchers in the use of some commonly discarded waste with biological origin named biosorbents.[7] The term of biosorption refers to an environmentally friendly technique similar to adsorption phenomena taking place essentially in the cell wall of microorganisms or on the surface of biomaterial.[8] This process is metabolism independent and accumulates chemicals onto the surface with some known mechanisms such as physical and chemical adsorption, electrostatic interaction, ion exchange, complexation, chelation, and microprecipitation.[7] The use of dead biomass is more advantageous than the use of live biomass because of its limited toxicity, the possibility of storage for a prolonged period of time and the fact that it does not require growth media and nutrients for its maintenance.[9] The mechanism of biosorption process, depends on many factors such as pollutant properties (species, ionic charge and size), type of biomass, its preparation, environmental conditions (pH, temperature, agitation rate, existence of competing organic or inorganic molecules, ionic strength) and surface properties of biomass.[10] In the literature, some fungal mycelica and bacterial biomass have been utilized to remove phenolic aromatics through adsorption. However, due to economic limitations, there is a growing interest in the use of available adsorbents such as rice husk and activated sludge.[11] Furthermore, some researchers have evaluated the potential of natural-based adsorbents such as coconut shell, tea leaves and fruit pits for the removal of organic compounds.[2,6] Sewage sludge is considered as a waste material, which can be treated and reused as a potential biosorbent for the removal of organic pollutants. Biological waste water treatment produces different sort of sludge within the individual process steps. Two important kind of sludge is activated and digested the sludge. Digested sludge is produced through anaerobic digestion process in the absence of oxygen but activated sludge is produced in biological aeration basins. The adsorptive features of municipal wastewater treatment sludge have not been investigated thoroughly for biosorption of organic compounds. Therefore, In this study, a comparison is made between dried activated sludge (DAS) and dried anaerobic digested sludge (DADS) to investigate the feasibility and biosorption capacity of both biosorbents for the removal of 4-chlorophenol (4-CP) in the same environmental conditions.

MATERIALS AND METHODS

Preparation of chemicals

All the chemicals were purchased from Merck Ltd. (>99% purity), Germany and use without further purification. The stock solution of 1000 mg/L was prepared by dissolving 4-CP (M = 128.56 g/mol) in deionized water. The 4-CP was solubilized by hot plate stirrer (IKA, labor Technik, USA) at 70°C The concentrations of prepared solutions varied between 5 and 30 mg/L in the sorption experiments and all working concentrations were obtained by diluting the stock solution with deionized water. The pH value of the solution in this study (2.0-11.0) was adjusted with pH meter (SCHOTT, CG 824, Germany) to the required value by adding 1M NaOH or 1M HCl solutions. All solutions were stored in the dark space at 4°C prior to use.

Preparation of biosorbent

The activated sludge was collected as slurry from the sludge return line and digested sludge was obtained from anaerobic digester in south municipal wastewater treatment plant (Isfahan, Iran). Both digested and activated sludge were dried at 105°C to constant weight and then grounded and sieved to obtain particle size under 0.35 mm. Thereafter, 50 g of the raw sludge biomass were added into 1 L of HCl solution (0.1 mol/L) and then stirring the mixture at 55 rpm for 30 min at 25 ± 0.5°C by an orbital shaker (SCHOTT, Germany).[12] After that, the acid-treated biomass was washed with deionized water several times until the pH did not change, and then digested and activated sludge were dried at 105°C.[4,13]

Experimental procedures

Sorption experiments were carried out in batch mode. Desired amount of the DADS and DAS with 100-mL solution of known 4-CP concentration were mixed in 250-mL conical

Table 1: Experimental parameters for 4-CP removal								
Tests	Biomass concentration (g/L)		Initial (4-CP) concentration (mg/L)		Initial pH value		Time (min)	
	DADS	DAS	DADS	DAS	DADS	DAS	DADS	DAS
Effect of biomass dosage	5-30	5-30	5-30	5-30	3	4	240	150
Effect of initial concentration	5-30	5-30	5-30	5-30	3	4	240	150
Effect of pH	5-10	5-10	5,10	5-10	2-11	2-11	90	90
Effect of time	20	20	20-40	20-40	3	4	5-360	5-360

DADS: Dried anaerobic digested sludge, DAS: dried activated sludge, 4-CP: 4-chlorophenol

flasks. 56 tests have done for each biosorbent. The effects of initial pH values, initial 4-CP and biomass concentration, as well as contact time on 4-CP removal, were studied as tabulated in Table 1. The flasks were agitated on a shaker at 250 rpm at room temperature (25 ± 1°C). After adsorption period, the adsorbents were separated by filter papers (Whatman, No. 4, Germany). The residual concentration of 4-CP were analyzed by measuring the absorbance of the red complex of 4-CP solutions by spectrophotometer (DR 2800. Hach, Germany). The amount of adsorption at equilibrium, q (mg/g) was obtained as follows:

$$q = \frac{[(C_0 - C_e).V]}{m} \tag{1}$$

Where C_0 and C_e are the initial and equilibrium concentration (mg/L); V is the volume of the solution (L); and m is the weight of the dry biomass used (g). Elemental composition test have been done to specify contents of both sludge (Elementar, vario Max, Germany). Table 2, represents the amount of carbon, nitrogen, hydrogen of two type of sewage sludge. As would be expected, digested sludge had lower content in carbon in comparison with activated sludge, which is attributed to methane emission during digestion phase.

RESULTS

Characterization of biosorbent

Scanning electron microscopy (SEM) is widely used to investigate the morphological features and surface characteristics of adsorbents. In this study, scanning electro-micrographs (Hitachi, S23000, Japan) show the surface texture and morphology of the DADS and DAS at the same magnification [Figure 1a and b]. It can be implied that both biosorbents have high porosity structure that is constituted by very small aggregated components.[7] The Fourier transform infrared (FT-IR) spectral analysis is important in identifying the different functional groups onto the biosorbent, which are responsible for biosorption of 4-CP. Figure 2 shows the FT-IR spectra (Ray leigh, WQF 5bA, China) of both biosorbents (DADS and DAS) before and after adsorption of 4-CP. The bands appearing at about 469/cm, 471/cm and 467/cm that are seen in all of the spectra, are related to bending vibrations of O-P-O in phosphate groups. The peaks located at 533/cm, 874/cm and 796/cm assigned to C-Cl stretching vibrations of aromatic ring are the great evidence for the absorption of 4-CP on the surface of sludge. These peaks are not observed in the witness spectrum. The absorptions around 1032/cm, 1037/

cm are due to stretching vibrations of P-O bond. The peaks at 1652/cm, 1639/cm, 1428/cm and 1450/cm are attributed to C-C bonds vibration of aromatic ring. The increasing intense of this peak after the absorption confirms the
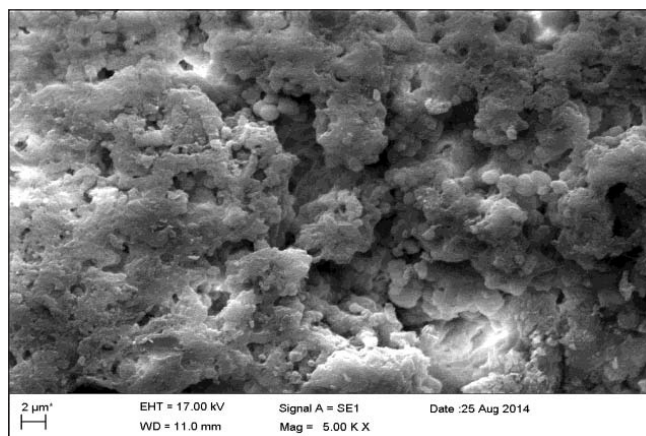

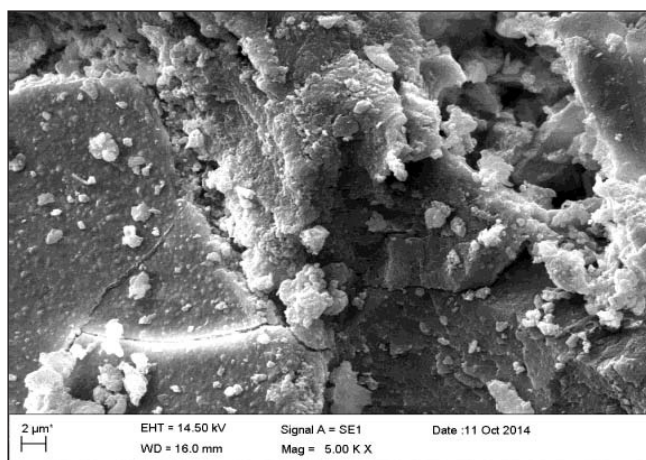**Figure 1a:** Scanning electron microscopy micrograph of dried anaerobic digested sludge

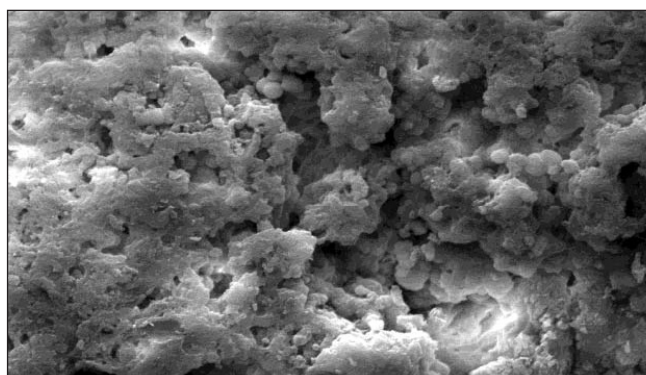**Figure 1b:** Scanning electron microscopy micrograph of dried activated sludge

Figure 2: Fourier transform infrared spectra of (a) noninteracted dried anaerobic digested sludge (DADS) (b) 4-chlorophenol (4-CP) interacted DADS (c) noninteracted dried activated sludge (DAS) (d) 4-CP interacted DAS

Table 2: Properties of two sewage sludge (CHNO elements)				
Sample	Carbon	Hydrogen	Nitrogen	Oxygen
Activated sludge	36.7	6.9	7.8	9.9
Digested sludge	27.49	5.01	10.39	7.8

CHNO: Carbon, Hydrogen, Nitrogen, Oxygen

existence of the 4-CP. The absorption peaks at 2854/cm and 2925/cm are related to stretching vibrations of aliphatic C-H bonds. The small peaks at 3277/cm, 3285/cm, 3374/cm, 3345/cm are attributed to vibrations of aromatic C-H bonds. The absorptions located at 3448/cm, 3512/cm, 3565/cm, 3548/cm and 3610/cm are assigned to O-H bonds of sludges and aromatic rings.

Effect of pH

The effect of initial pH on the equilibrium uptake capacity of 4-CP by DADS and DAS at pH 2.0-11.0 and 25 ± 1°C is shown in Figure 3. The biosorption of 4-CP significantly influenced by pH. Different initial concentration of 4-CP were selected to investigate the effect of initial concentration on uptake capacity. Similar trends were observed for two different initial concentrations. The maximum removal of 4-CP was obtained at initial pH of 3 for DADS and 4 for DAS. An increase or decrease in the pH from these optimum values resulted in a reduction in the biosorption capacity of 4-CP.

Effect of dosage and initial concentration

The dependence of 4-CP biosorption on bisorbents dose was investigated by varying the amount of adsorbents from 5 to 30 g/L while keeping other parameters constant. The maximum sorption capacity of 0.94 mg/g for DADS and 1.537 for DAS was observed, when 30 mg/L of 4-CP and 5 g/L of both bisorbents were used. With increasing biomass dosage from 5 to 30 g/L, a decreasing trend in sorption capacity was observed. From Figure 4, it is apparent that the removal of 4-CP increase rapidly with an increase in the dosage of adsorbent due to greater availability of binding sites of the biosorbent.[3,4] The maximum removal was 96.6% for DADS and 99.86% for DAS when 5 mg/L of 4-CP and 30 g/L of DADS and DAS were used. As seen in Figure 4a and b the equilibrium sorption capacity of DADS and DAS increased with increasing initial 4-CP concentration from 5 to 30 mg/L. In this figure column, bars are related to removal of 4-CP and solid lines biosorbent capacity.

Contact time

The relationship between contact time and 4-CP sorption on DADS and DAS at different initial 4-CP concentration (20 mg/L, 40 mg/L) is presented in Figure 5. Biosorption rate of 4-CP was very high at the beginning of the process for both biosorbents and saturation level was gradually reached within 4 h for DADS and 2.5 h for DAS.
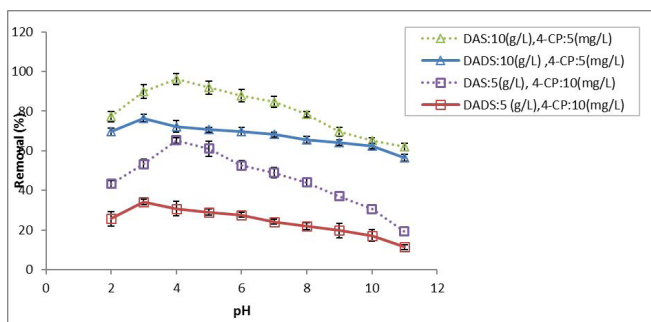

Figure 3: Effect of initial pH on sorption capacity of 4-chlorophenol by dried activated sludge and dried anaerobic digested sludge (temperature: 25 ± 1°C, agitation: 250 rpm, contact time: 90 min)

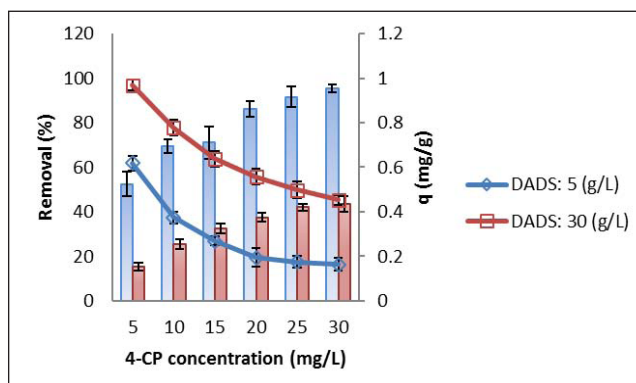**Figure 4a:** Effect of initial concentration of 4-chlorophenol on sorption capacity of dried anaerobic digested sludge (temperature: 25 ± 0.5°C, agitation: 250 rpm, pH: 3, contact time: 240 min)

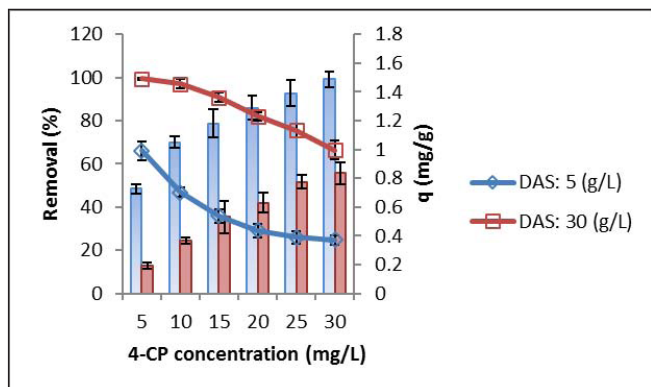**Figure 4b:** Effect of initial concentration of 4-chlorophenol on sorption capacity of dried activated sludge (temperature: 25 ± 0.5°C, agitation: 250 rpm, pH: 3, contact time: 240 min)
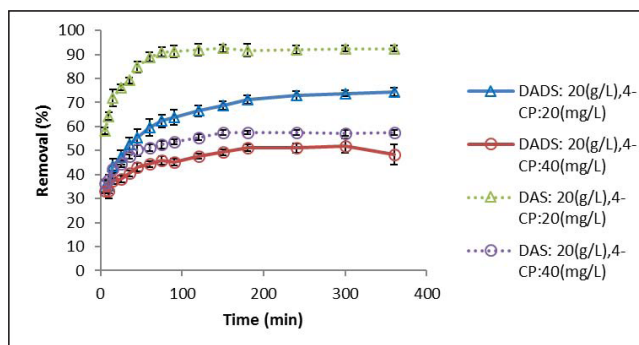

Figure 5: Effect of contact time on sorption capacity of 4-chlorophenol by dried anaerobic digested sludge and dried activated sludge (temperature: 25 ± 0.5°C, agitation: 250 rpm, pH: 3, dose: 20 g/L)

DISCUSSION

Effect of pH

The pH has a significant effect on the degree of ionization of 4-CP as well as the surface properties of the biosorbents. Previous studies have found that isoelectric point of DADS and DAS would be usually between 1 and 3. For the pH values below isoelectric point the overall charge on the biosorbent surface became positive. As the pH increased, however, the overall surface charge on the cells became negative and the removal efficiency decreased. The amount of adsorbed 4-CP seemed to be related to the dissociation constant (pK_a), which is 9.41 for 4-CP. When pH is not more than one unit above pKa values of 4-CP, Nondissociated forms activated by the OH^- and Cl^- dominated the overall sorption of chlorinated phenols on organic sorbent. When pH is greater than pKa values of 4-CP, negatively charged ionized forms dominate in the solution.[10,14] The optimum pH (pH: 3.0) is well in agreement with previous studies carried out by granular anaerobic sludge for DADS.[15] However, similar studies carried out by other researchers have shown different results for optimum pH for biosorption process by activated sludge.[8,16]

Dried activated sludge and dried anaerobic digested sludge dosage

With increasing biomass dosage from 5 to 30 g/L, a decreasing trend in sorption capacity was observed. The drop in adsorption capacity was due to binding sites of the adsorbent remained unsaturated during the adsorption process. Adsorption studies carried out using different kinds of biosorbent showed a similar trend with a change in biomass concentration.[17] From Figure 4, it is apparent that the removal of 4-CP increase rapidly with an increase in the dosage of adsorbent due to greater availability of binding sites of the biosorbent.[3,4] The maximum removal was 96.6% for DADS and 99.86% for DAS when 5 mg/L of 4-CP and 30 g/L of DADS and DAS were used.

Initial concentration of 4-chlorophenol

By increasing the initial concentration of 4-CP, all mass transfer resistance will be decreased and, therefore, the rate at which adsorbate molecules pass from the bulk solution to the adsorbent surface will be increased. The increasing trend of sorption capacity can be justified due to a higher probability of collision between 4-CP molecules and biosorbents surfaces.[10] As seen in Figure 4a and b the equilibrium sorption capacity of DADS and DAS increased with increasing initial 4-CP concentration from 5 to 30 mg/L. Similar results were observed by other researchers by changing adsorbate concentration.[3,15]

Isotherms study

Sorption isotherms represent the amount of sorbate at the surface of sorbent material present in the solution.[6,18] Sorption isotherms are often used as empirical models, which are obtained from measured data by means of regression analysis. Two classical adsorption models including Langmuir and Freundlich isotherms are most frequently employed.[7,19] In this study, these two models were used to describe the relationship between the amount of 4-CP adsorbed and its equilibrium concentration in solution at different dosages of DADS and DAS. The equation of these models and their linear forms are shown in Table 3. All the constant of these two models were estimated by a linear regression, and the results were summarized in Table 4.

Langmuir

The Langmuir model assumes the surface of the adsorbent is homogenous, and a monolayer coverage of surface could happen. Furthermore, in the Langmuir model, there are no interactions between adsorbate molecules on adjacent sites and all site on the surface are equivalent.[15] In this equation C_e is the 4-CP equilibrium concentration in the solution (mg/L), Q_e is the equilibrium 4-CP uptake on the biosorbent (mg/g), Q_{max} is the maximum biosorption capacity (mg/g) and K_L is Langmuir constant (L/mg). The Langmuir model

Table 3: Nonlinear and linear forms of isotherm models

Isotherms	Equation	Liner form
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e$
Langmuir	$q_e = \dfrac{Q_m K_L C_e}{1 + K_L C_e}$	$\dfrac{C_e}{q_e} = \left(\dfrac{1}{K_L Q_m}\right) + \left(\dfrac{1}{Q_m}\right)C_e$

Table 4: Isotherm constant parameters and correlation coefficients calculated for adsorption of 4-CP

Dose	Freundlich						Langmuir					
	DADS			DAS			DADS			DAS		
	1/n	K_f	R^2	1/n	K_f	R^2	Q_m	K_L	R^2	Q_m	K_L	R^2
5	0.180	0.523	0.99	0.19	0.81	0.97	1.01	0.443	0.99	1.605	0.46	0.99
10	0.179	0.48	0.98	0.183	0.644	0.98	0.869	0.705	0.99	1.153	0.83	0.99
15	0.189	0.384	0.99	0.212	0.544	0.99	0.704	0.802	0.99	1.015	0.95	0.99
20	0.20	0.316	0.95	0.214	0.478	0.99	0.613	0.701	0.96	0.856	1.27	0.96
25	0.20	0.271	0.98	0.228	0.428	0.99	0.534	0.665	0.984	0.763	1.45	0.98
30	0.22	0.234	0.99	0.269	0.358	0.99	0.469	0.712	0.984	0.692	1.24	0.98

DADS: Dried anaerobic digested sludge, DAS: dried activated sludge, 4-CP: 4-chlorophenol

has a high R^2 value, indicating a formation of 4-CP covering the biosorbent surface. The suitability of the adsorbent for adsorbate can be expressed using the hall separation factor (R_L, dimensionless) which can be calculated in the following equation:

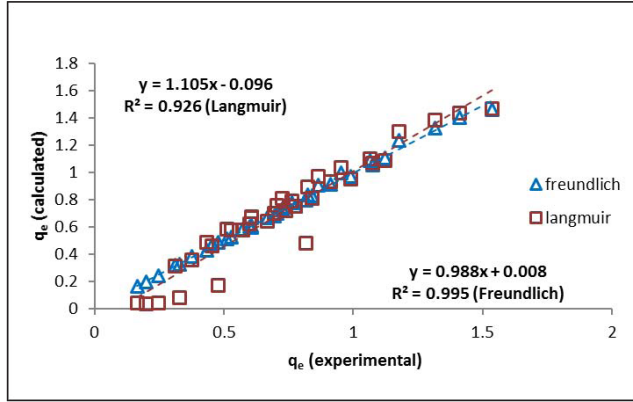$$R_L = \frac{1}{1 + K_L C_0} \qquad (2)$$

Where, K_L and C_0 are Langmuir constant (L/mg) and initial dye concentration (mg/L), R_L indicates the nature of adsorption. The R_L parameter is considered as a more reliable indicator of the adsorption. The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$), respectively.[14] All the R_L values of 4-CP adsorption lie between the ranges of 0.423-0.702, indicating that the biosorption process was favorable.
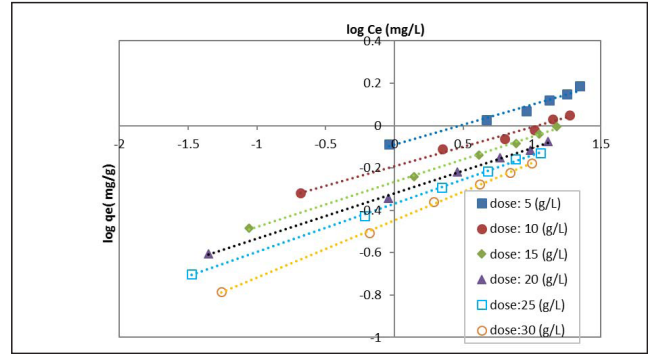

Figure 6: Comparison among experimental data, Langmuir and Freundlich output

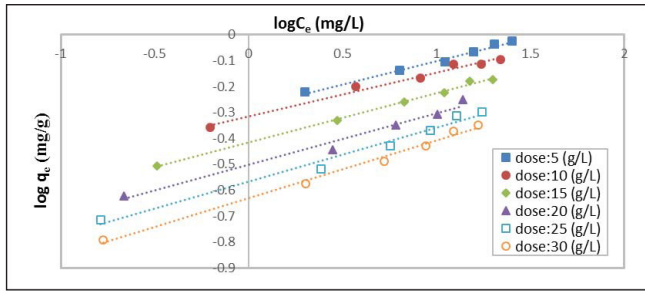**Figure 7a:** Freundlich sorption isotherm for dried activated sludge (temperature: 25 ± 1°C, pH: 3, contact time: 240 min)

Figure 7b: Freundlich sorption isotherm for dried anaerobic digested sludge (temperature: 25 ± 1°C, pH: 3, contact time: 240)

Table 5: Nonlinear and linear forms of kinetic models

Kinetic	Equation	Liner form
Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	$q_e = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$
Intraparticle diffusion	—	$q_t = K_{dif}t^{0.5} + C$

Table 6: Kinetic constant parameters and correlation coefficients for 4-CP adsorption

Kinetic	Parameter	4-CP concentration (mg/L)					
		20	20	30	30	40	40
		DADS	DAS	DADS	DAS	DADS	DAS
Pseudo-first order	k_1	0.016	0.05	0.011	0.025	0.008	0.016
	$q_{e\,(cal)}$	0.401	0.538	0.413	0.359	0.423	0.448
	R^2	0.99	0.985	0.99	0.906	0.98	0.965
	r^2	0.98	—	0.99	—	0.99	—
Pseudo-second order	k_2	0.101	0.204	0.108	0.101	0.116	0.108
	$q_{e\,(cal)}$	0.755	0.960	0.926	1.098	1.041	1.165
	R^2	0.99	0.999	0.99	0.988	0.99	0.996
	r^2	0.91	—	0.89	—	0.92	—
Elovich	α	0.52	4.529	1.25	3.295	2.93	3.138
	β	2.56	9.09	1.31	8	0.88	7.30
	R^2	0.98	0.971	0.95	0.942	0.97	0.971
	r^2	0.518	—	0.536	—	0.532	—
Intraparticle diffusion	K_{dif}	0.034	0.034	0.032	0.041	0.031	0.045
	C	0.297	0.570	0.485	0.574	0.612	0.615
	R^2	0.95	0.851	0.98	0.952	0.98	0.956

DADS: Dried anaerobic digested sludge, DAS: dried activated sludge, 4-CP: 4-chlorophenol

Freundlich

The Freundlich equation is obtained by assuming that the surface is heterogeneous. That means, adsorption energy is distributed and sites having the same energy are grouped together into one patch. In this equation K_f (L/g) and n (dimensionless) are indicators of adsorption capacity and adsorption intensity of the sorbent.[10] The plot of $\log q_e$ versus $\log C_e$ gave a straight line with a slope of $1/n$ and intercept of $\log K_f$. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its values get closer to zero.[20] Figure 6 (a comparison between experimental and model calculated data) show that Freundlich model exhibited a slightly better fit to the biosorption data than the Langmuir model in the dosage range studied. Also, earlier studies have indicated that, adsorption equilibrium of organic pollutants, such as phenols and chlorophenols, followed the Freundlich isotherm better than the Langmuir one.[17,21] Figure 7a and b shows a linear form of Freundlich model for biosorption of 4-CP.

Biosorption kinetic study

Adsorption kinetic models were applied to investigate the sorption dynamics of 4-CP molecules on the DADS and DAS. Experimental data were fitted by kinetic models such as pseudo-first, pseudo-second and Elovich equations. In addition, intra particle diffusion was further tested to determine diffusion mechanism of the adsorption process. Table 5 shows the nonlinear and linear forms of these kinetic equations. All the constant of these models were estimated by a linear regression, and the results were listed in Table 6. The results

suggested that: The second order adsorption mechanism was predominant for DAS and first order adsorption model fitted well for DADS. Results were shown in Figure 8a and b.

Intra particle diffusion (Weber-Morris model)]

Intra particle diffusion model was proposed by Weber and Morris. Based on this model, there is an empirical functional relationship in most adsorption processes, where uptake varies almost proportionally with $t^{0.5}$ rather than with the contact time (t).[4,19] If intraparticle diffusion occurs, then q versus $t^{0.5}$ will be linear, and if the plot of q versus $t^{0.5}$ passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved.[4,6] In this model, q_t (mg/g) is the amount adsorbed at time t (min), K_{id} (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant and C is the value of intercept which gives an idea about the boundary layer thickness, that is, the larger intercept, the greater is the boundary effect. The values of K_{id} and C were obtained by the plot of q_t versus the square root of time and are listed in Table 5 for both adsorbents (DADS and DAS). As shown in Figure 9a and b, the plots present a linear relationship but did not pass through the
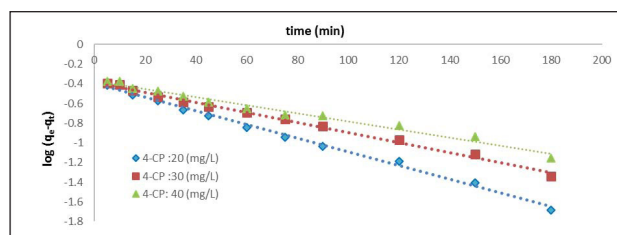

Figure 8a: Pseudo-first order model for biosorption of 4-chlorophenol by dried anaerobic digested sludge (temperature: 25 ± 0.5℃, agitation: 250 (rpm), pH: 3, contact time: 240 (min), dosage: 20 g/L)

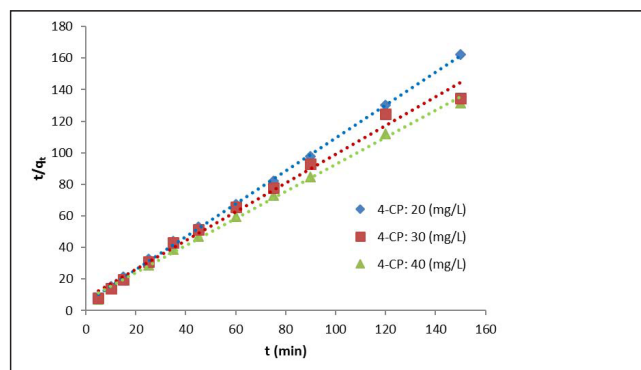**Figure 8b:** Pseudo-second order model for biosorption of 4-chlorophenol by dried activated sludge (temperature: 25 ± 0.5℃, agitation: 250 (rpm), pH: 4, contact time: 240 (min), dosage: 20 g/L)
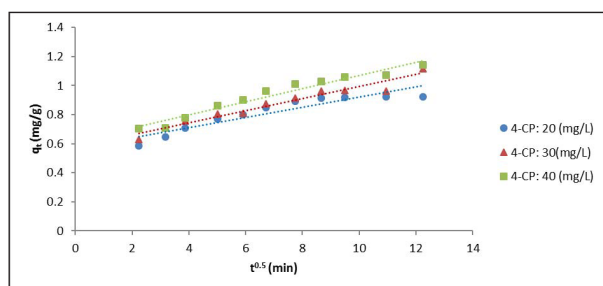

Figure 9a: Intra particle diffusion plot for adsorption of 4-chlorophenol by dried activated sludge (temperature: 25 ± 1℃, agitation; 250 rpm, pH: 3, contact time; 240 (min), dosage: 20 g/L)
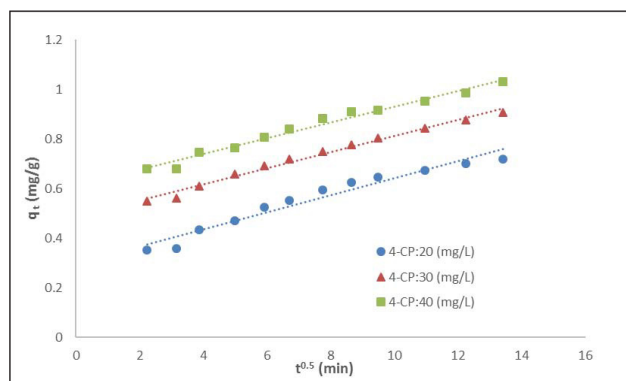

Figure 9b: Intra particle diffusion plot for adsorption of 4-chlorophenol by dried anaerobic digested sludge (temperature: 25 ± 1℃, agitation; 250 rpm, pH: 4, contact time; 240 (min), dosage: 20 g/L)

origin. This suggested that intra particle diffusion was not the only rate controlling step and some other rate limiting steps may be involved and may affect the adsorption of 4-CP. Removal of 2-chlorophenol by low-cost coir pith carbon were investigated, kinetic studies of this research showed that some other mechanism along with intra particle diffusion is also involved.[19]

CONCLUSION

The present study led to the following conclusions: The maximum adsorption capacity for DADS was 0.94 mg/L and 1.537 mg/L for DAS. The optimum pH for DADS was 3 and 4 for DAS. It takes 4 h for DADS and 2.5 h for DAS to reach equilibrium condition. IBM SPSS statistics (version 20, USA) software was used for statistical analysis between DADS and DAS. 2-sample independent test was applied to have a comparison between average removal of 4-CP by DADS and DAS. Results showed, there is a meaningful difference between dads and DAS for the removal of 4-CP ($P < 0.05$). The SEM technique verified the porous structure of biosorbent surfaces. The interactions between 4-CP and the biosorbent surface of DADS and DAS were confirmed by FT-IR test. Also, functional groups for DAS were as the same for DADS. The biosorption equilibrium data of both biosorbent followed Freundlich equation, and kinetic studies showed that pseudo-first-order model for DADS and pseudo-second order model for DAS can describe appropriately adsorption process. The Weber-Morris model suggested that some other mechanisms in addition to intra particle diffusion may affect biosorption process.

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Conflicts of interest
There are no conflicts of interest.

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