Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.3331

Taylor & Francis
Taylor & Francis Group

45 (2012) 263–275
July

Removal of anionic surfactant sodium dodecyl sulphate from aqueous solution by adsorption onto pine cone biomass of *Pinus Radiate:* equilibrium, thermodynamic, kinetics, mechanism and process design

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Received 25 September 2011; Accepted 6 November 2011

ABSTRACT

This study was undertaken to evaluate the adsorption potential of a natural, low-cost agricultural by-product adsorbent, Pine cone (*Pinus Radiate*), to remove sodium dodecylsulfate (SDS) from aqueous solution. It was found that the extent of SDS adsorption by pine cone biomass increased with initial surfactant concentration and contact time but decreased with increasing solution pH, amount of adsorbent, and temperature of the system. These studies also suggested that the electrostatic forces and surfactant self-assembly are dominant mechanisms governing this pH dependent adsorption process. Overall, kinetic studies showed that the surfactant adsorption process followed pseudo-second-order kinetics based on pseudo-first-order and intraparticle diffusion models. The different kinetic parameters including rate constant, half adsorption time, and diffusion coefficient were determined at different physicochemical conditions. Equilibrium data were fitted by both the Langmuir isotherm and Freundlich adsorption isotherm. The maximum monolayer adsorption capacity of pine cone biomass was 95.75 mg g^{-1} at 20°C. The value of separation factor, R_L from Langmuir equation and "n" from Freundlich also indicated favourable adsorption. Thermodynamic parameters such as ΔG^0, ΔH^0, and ΔS^0 were calculated. A single-stage batch absorber design for the SDS adsorption onto pine cone biomass also presented based on the Freundlich isotherm model equation.

Keywords: Surfactant; *Pinus radiate*; SDS adsorption; Kinetic model; Isotherm; Process design

1. Introduction

Surfactants are one of the major ingredients in cosmetic products and detergents for industrial and household cleaning. There are four classes of surfactants (cationic, anionic, amphoteric and non-ionic) based on the ionic charge (if present) of the hydrophilic portion of the surfactant in an aqueous solution [1]. The anionic surfactants, including sodium dodecyl sulfonates (SDS), are major constituents of synthetic detergents, which are widely used in various industrial processes, such as in paper industries, cosmetics, food processing, laundry, vehicles washing, electroplating, textile industry, biotechnology [2,3]. Additionally, SDS is employed in mineral flotation and in oil recovery processes. Therefore the non-reacted surfactant amount from such extensive applications has produced a large industrial liquid effluents and their treatment is usually difficult, expensive and problematic in wastewater treatment plants. Surfactants are one of the most common organic pollutants

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characterized with very high potential to enter the environment, primarily in aqueous solutions, via wastewater discharge [1]. Surfactants are harmful to human beings, fishes and vegetation. They are responsible for causing foams in rivers and effluent treatment plants and affect water quality [4]. Consequently, treatment process is necessary in order to remove or reduce surfactants from industrial and domestic wastes. A range of technologies have been developed and used for the removal of surfactants from wastewater such as adsorption, coagulation/flocculation, advanced oxidation, ozonation, membrane filtration, liquid–liquid extraction and various biological methods [1,2,4,5]. All processes have their own limitations. An economical and sustainable removal of surfactants and organics remains an important problem despite of a number of systems have been developed with adsorption technique. Adsorption is a very effective separation technique and considered superior to other techniques for water treatment in terms of initial cost, simplicity of design, and ease of operation and insensitive to toxic substances [6–8]. Adsorption of anionic surfactant has been investigated by numerous adsorbents like activated carbon, silica gel, clay minerals, soil, sand, kaolinite [3,9], alumina [4], modified zeolite with CTAB [2], sepiolite [10], rice husk [5] and also on cellulosic surface [11]. A commonly used adsorbent, activated carbon has a high capacity for the removal of surfactant/organics. However, activated carbon is expensive and difficult to regenerate which significantly increases the cost of the wastewater treatment. Thus the search for new and innovative treatment techniques has focused on the adsorption capacities of other adsorbents, such as agricultural by-products and lignocelluloses residues which are readily available and more economical and sustainable[12]. Recently some agricultural and forestry products and wastes have been recognized as new adsorbent for the removal of inorganic and organics [13]. However there are only very few reports about the use of agricultural by-products for the removal of anionic surfactants like SDS.

Large quantities of pine cones are produced annually as agricultural by-product throughout the world. The ovulate cone is the well-known cone of the *Pinus and* other conifers. Each cone is composed of an axis upon which are borne, in a spiral fashion, a large number of woody scales. The scales of the mature cone are composed of epidermal and sclerenchyma cells which contain cellulose, hemicelluloses, lignin, rosin and tannins in their cell walls [14]. These scale of this ovulate cone as cone biomass is a waste itself and a readily available adsorbent which is tested here to remove SDS from its aqueous solution. There are only few studies such as *Pinus sylvestris* have been used to remove chromium (VI) from its aqueous solution [14] and reactive red dye [15] has been reported. Removal of copper (II) from aqueous solution by pine cone powder as biosorbent has also been reported by Ofomaja et al. [16]. Phenol has been removed by *Pinus pinaster* [12]. However, no work has been reported on the use of cone biomass of *pinus Radiate* as an effective adsorbent for the removal of anionic surfactant, SDS from aqueous solution. In our previous work, it was found that pine cone biomass was able to effectively remove the cationic dye, methylene blue from its aqueous solution due to its particular structure [13]. Therefore, the present study is aimed to investigate SDS adsorption on ovulate cone biomass of *Pinus radiate* and intend to develop an effective, economical and sustainable adsorbent. *Pinus Radiate* is one species of pine tree and it is available throughout Australia as well. This present research work will explore the mechanism of adsorption and adsorption kinetics of SDS adsorption by *Pinus radiate* and will determine the various physicochemical controlling factors on the rate of adsorption and also on the capacity of adsorbent. The effect of solution pH, initial surfactant concentration, adsorbent dose, and temperature on SDS adsorption has been investigated. Further various thermodynamic parameters such as Gibbs free energy change (ΔG^0), heat of adsorption (ΔH^0), entropy change (ΔS^0) and activation energy (A) were also analysed. Finally, a single-stage batch adsorber has been designed for the removal of surfactant by *pinus radiate* based on the equilibrium data obtained.

2. Materials and methods

2.1. Adsorbent

Pine tree cones (*Pinus radiate*) were obtained from the campus of Curtin University, Perth Western Australia and it was collected between February and March 2010. The cones were washed thoroughly with distilled water to remove impurity such as sand and leaves, the washed cones as cone biomass were then dried at 70°C for 24 h in an oven. The scales on the dried cones were then removed and ground in a crusher. The resultant ground pine cone powders were passed through British Standard Sieves (BSS) of 150 μm and then collected in an airtight plastic container and used for analysis as well as for adsorption experiments. Pine cone biomass powder was analysed by the Spectrum 100 FT-IR Spectrometer to determine functional groups. A Scanning Electron Microscope (EVO 40) was used for the information of the surface morphological structure of pine cone before and after adsorption. Particle size of pine cone powder was measured by Malvern Hydro 2000S master Sizer, Malvern Instruments Ltd., UK.

2.2. Adsorbate and other chemicals

All chemicals used were of analytical grade. The anionic surfactant, SDS (M = 288.38 g mol^{-1}) was obtained from Sigma Aldrich with 99.99% purity. It was used without further purification. Fig. 1 shows the chemical structure of SDS. The surfactant solutions were prepared in a standard 1000 ml volumetric flasks, surfactants were weighed on mass basis and emptied into the volumetric flask and then double distilled water was used to complete the solution to the final weight. After the preparation of the stock solution, it was diluted to obtain the various working solutions. The pH of the solutions was adjusted by addition of either 0.1 M HCl or 0.1 M NaOH solutions respectively. All sample bottles and glassware were cleaned, and then rinsed with deionised water and oven dried at 60°C.

The concentration of the residual surfactant was measured using conductivity meter by withdrawing samples at fixed time intervals, centrifuged and the supernatant was analysed for surfactant concentration. Calibration curve was plotted between sp. conductance and concentration of the SDS solution to obtain ap. conductance-concentration calibration plot. Also measured sp. conductance of blank solution (without surfactant) each time which was subtracted from final sp. conductance value.

2.3. CMC measurement

The critical micellar concentration (CMC) value was obtained through a conventional plot of the surface tension measurement versus the surfactant concentration which is shown in Fig. 2. The CMC concentration corresponds to the point where the surfactant first shows the lowest surface tension. The surface tension remains relatively constant after this point. The CMC of SDS was 7.1 mM at 20°C. The surface tension measurements were carried out by Wilhelmy plate method in a surface tensiometer (from KSV, Finland) at constant temperature.

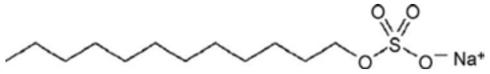

Fig. 1. Chemical structure of sodium dodecyl sulfate [1].

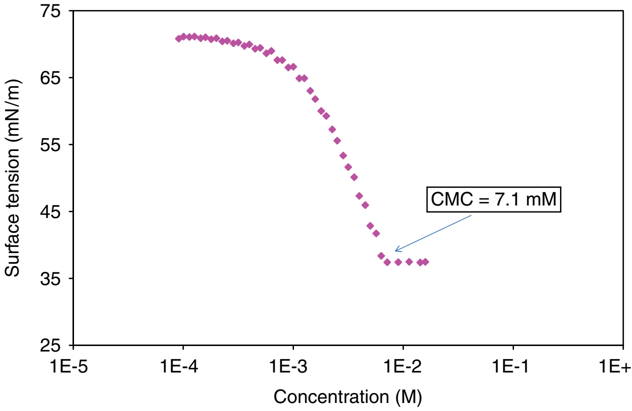

Fig. 2. Plot of Surface tension versus SDS concentration.

2.4. Adsorption experiment

2.4.1. Kinetic experiments

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 75 ml of aqueous SDS solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at a constant temperature using Thermo line scientific Orbital Shaker Incubator at 120 rpm at 20°C temperature for 180 min. At predetermined time, the bottles were withdrawn from the shaker and the residual SDS concentration in the reaction mixture was analysed by centrifuging the reaction mixture and then measuring the sp. conductance of the supernatant solution. Surfactant concentration in the reaction mixture was calculated from the calibration curve. Adsorption experiments were conducted by varying initial solution pH, contact time, adsorbent dose, initial SDS concentration and temperature under the aspect of adsorption kinetics, adsorption isotherm and thermodynamic study.

The amount of SDS adsorbed onto pine cone powder biomass at time t, q_t (mg g^{-1}) was calculated by the following mass balance relationship:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

And SDS removal efficiency i.e., % of adsorption was calculated as:

$$\%\ \text{Adsorption} = \frac{C_0 - C_t}{C_0} 100 \tag{2}$$

where C_0 is the initial SDS concentration (mg l^{-1}), C_t is the concentration of SDS at any time t, V is the volume of solution (l) and m is the mass of pine cone powder (g).

All measurements are, in general, reproducible within ±10%.

2.4.2. Isotherm experiments

Equilibrium adsorption studies were conducted by contacting 75 ml of SDS solutions of different initial concentration of 10, 20, 30, 40, 50, 60, 70 and 80 ppm with 20 mg of pine cone powder in 250 ml conical flasks for a period of 3.5 h which was more than sufficient to equilibrium time. The method was as per subsection 2.4.1.

The initial concentration of surfactant SDS was selected based on concentrations often found in industrial effluents.

2.5. Theory

2.5.1. Adsorption isotherm

To simulate the adsorption isotherm, two commonly used models, the Freundlich [17] and Langmuir [18] were selected to explicate SDS–pine cone interaction.

2.5.1.1. Freundlich isotherm The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed as:

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \tag{3}$$

where q_e is the amount of SDS adsorbed per unit of adsorbent at equilibrium time (mg g^{-1}), C_e is equilibrium concentration of SDS in solution (mg l^{-1}). K_f and n are isotherm constants which indicate the capacity and the intensity of the adsorption respectively [13].

2.5.1.2. Langmuir isotherm The linearized form of Langmuir can be written as [19]:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_a q_m}\right) + \frac{C_e}{q_m} \tag{4}$$

The Langmuir constants, q_m (maximum adsorption capacity) (mg g^{-1}) and K_a (values for Langmuir constant related to the energy of adsorption (l mg^{-1})) are predicted from the plot between C_e/q_e versus C_e.

2.5.2. Adsorption kinetics

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the transient behaviour of the SDS adsorption process was analysed using the pseudo first order, pseudo second order and intraparticle diffusion model which are explained as follows.

2.5.2.1. Pseudo-first-order model The integral form of the pseudo-first-order model generally expressed as [13,20]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5}$$

where q_t and q_e represents the amount of SDS adsorbed (mg g^{-1}) at any time t and at equilibrium time respectively and k_1 represents the adsorption first-order rate constant (min^{-1}) and t is the contact time (min). The adsorption rate constant k_1 were calculated from the plot of log $(q_e - q_t)$ against t.

2.5.2.2. Pseudo-second-order model The adsorption data was then analyzed in terms of pseudo-second-order mechanism, described by [8,20]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}).

Integrating and applying boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

A plot between t/q_t versus t gives the value of the constants k_2 (g mg^{-1} h^{-1}) and also q_e (mg g^{-1}) can be calculated.

The constant k_2 is used to calculate the initial sorption rate h, at $t \to 0$, as follows:

$$h = k_2 q_e^2 \tag{8}$$

thus the rate constant k_2, initial adsorption rate h and predicted q_e can be calculated from the plot of t/q versus time t using Eq. (7).

2.5.3. Adsorption mechanism

Intra-particle diffusion model is commonly used for identifying the adsorption mechanism for design purpose. According to Weber and Morris [21] for most adsorption processes, the uptake of SDS varies almost proportionately with $t^{1/2}$ rather than with the contact time and can be represented as follows:

$$q_t = K_{id\,=}\, t^{0.5} + I \tag{9}$$

where q_t is the amount adsorbed at time t and $t^{0.5}$ is the square root of the time and K_{id} [(mg/g^{-1}) $min^{0.5}$] is the rate constant of intraparticle diffusion.

2.5.4. Thermodynamic study

Thermodynamic parameters such as Gibbs free energy (ΔG^0), enthalpy change (ΔH^0) and change in entropy (ΔS^0) for the adsorption of SDS on pine cone biomass has been determined by the following equations [13]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{10}$$

$$\log\left(\frac{q_e}{C_e}\right)=\frac{\Delta S^0}{2.303R}+\frac{-\Delta H^0}{2.303RT} \tag{11}$$

where q_e is the amount of SDS adsorbed per unit mass of pine cone (mg g^{-1}), C_e is equilibrium concentration (mg l^{-1}) and T is temperature in K and R is the gas constant (8.314 J mol^{-1} K^{-1}).

3. Results and discussion

3.1. Characterization of pine cone biomass

The physical and chemical characteristics of adsorbents are important for understanding the adsorbate binding mechanism on the biomass surface [13]. Characterization of the structure and surface chemistry of adsorbent is of considerable interest for the development of adsorption and separation processes. One important characteristics of an adsorbent is the surface functional groups present which are largely characterized by the FTIR spectroscopy method. Pine cone is composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignin, rosin, and tannins in their cell walls which contains polar functional groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and other groups [16]. These groups will form active sites for sorption on the material surface. As per our previous study, Fig. 3 shows the FTIR spectra of pine cone biomass [13]. Several peaks were observed from the spectra (Fig. 3) indicating that pine cone is composed of various functional groups which are responsible for binding of SDS molecules. The peaks at 3301.28 cm^1 indicates O-H stretching vibrations and spectra bands observed at 2926.87 cm^{-1} represent vibration of CH$_n$ especially due to C–CH and C–CH$_2$ bonds. The peak at 16.7.67 cm^{-1} corresponds to C=O and vibration of C=C. The peak at 1369.55 cm^{-1} corresponds to N-alkyl ted aromatic amines and peaks at 1,264.25 cm^{-1} indicates C–N stretching with amine or C–O vibration of carboxylic acid [22]. The peaks between 1052.93 to 765.45 cm^{-1} may be assigned to the –C–C– and –CN stretching respectively. Similar type of FTIR spectra of pine cone has been reported by other investigators [16,22].

Scanning electron micrograph (SEM) of pine cone biomass before and after adsorption is shown in Figs. 4a and b respectively. The availability of pores and internal surface is clearly displayed in the SEM picture of the pine cone biomass before adsorption and the coverage of the surface and the pores by the adsorbed SDS is shown in Fig. 4b. Basically, the porous structure that appears in Fig. 4a gets blurred in Fig. 4b because of adsorption. The particle size distribution of pine cone biomass for which specific surface area was 0.213 m^2 g^{-1}. By taking the average surface weighted mean of each of the trials, the mean particle size for the pine cone biomass used was 28.19 μm.

3.2. Effect of initial solution pH on SDS surfactant adsorption kinetic experiment

The pH of the aqueous solution in which sorption is being conducted is an important controlling parameter

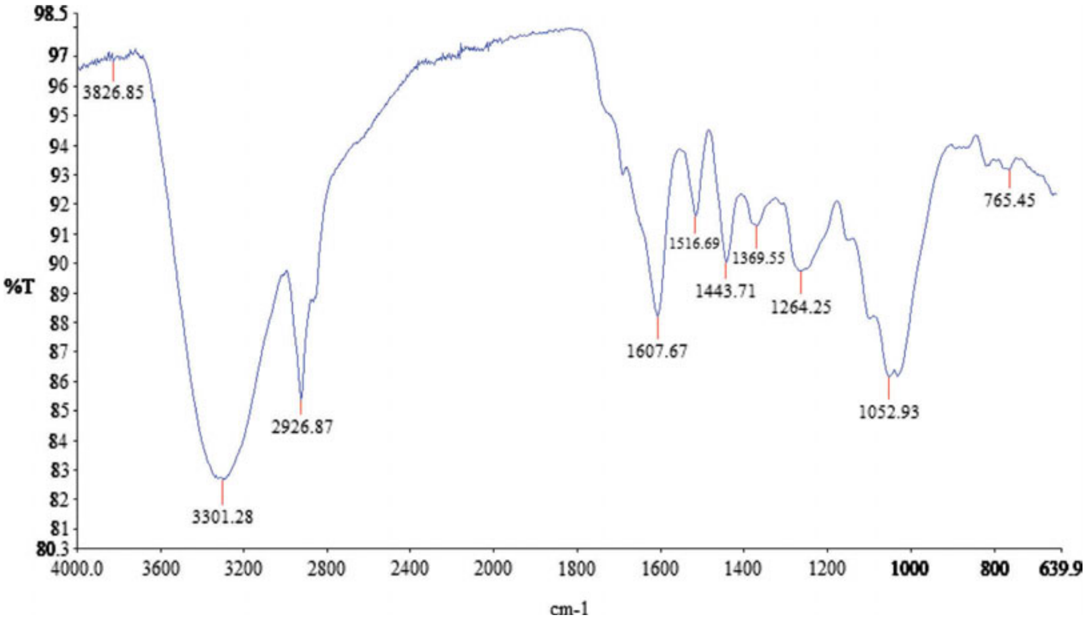

Fig. 3. FTIR Spectra of pine cone biomass [13].

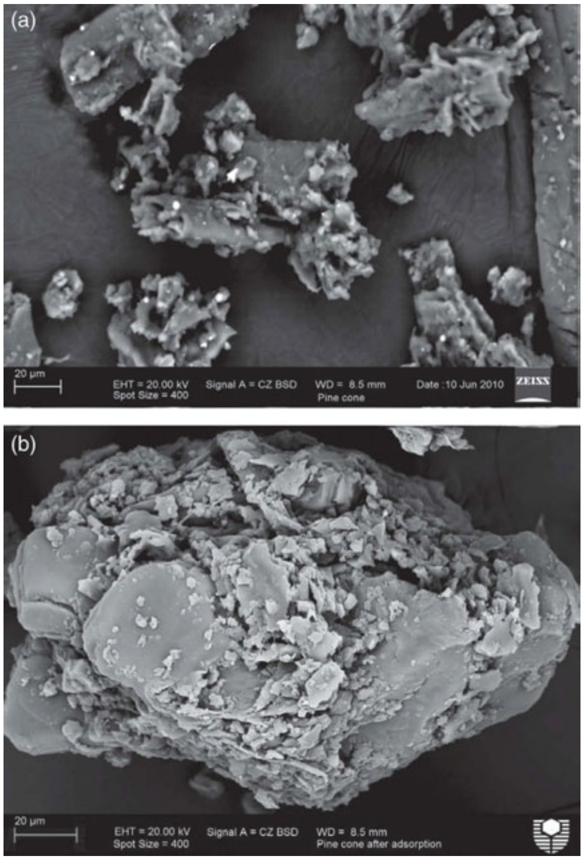

Fig. 4. (a) SEM of pine cone biomass before adsorption. (b) SEM of same pine cone biomass after methylene blue adsorption.

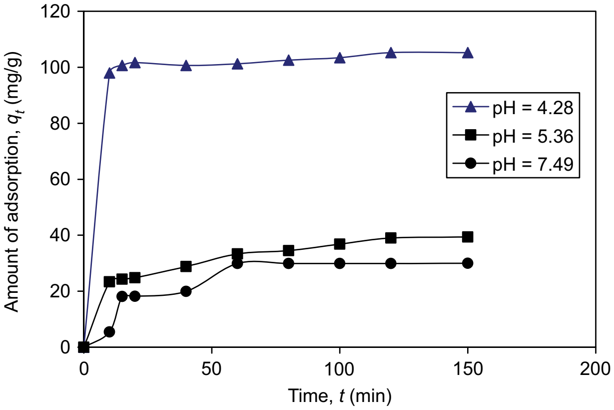

Fig. 5. Effect of initial solution pH on the adsorption of SDS onto pine cone powder: mass of adsorbent = 20 mg; volume of SDS solution = 75 ml; initial SDS concentration = 50 ppm; temperature = 20°C; shaker speed = 125 rpm.

in the adsorption process [16]. The effect of pH was studied in the range of 4.28 to 7.49. Lower pH is favourable for SDS adsorption. Adsorbed mass SDS consistently decreased with increasing solution pH (Fig. 5). Also, the amount of SDS adsorption increases with time (Fig. 5). The percentage removal of SDS was also found to decrease when the solution pH was increased from pH 4.28 to pH 7.49 for which plot are not presented here. The adsorption of ionic surfactants on charged surface is generally different from ordinary adsorption process. The ionic surfactant molecules form monolayer or bilayer on solid charged surface depending upon the surfactant concentration [4]. The dominant adsorption mechanisms between the SDS molecules and the pine cone biomass surface are thought to involve head group electrostatics and tail group lateral hydrophobic interactions [23]. At low concentrations, below CMC, SDS ions are bound to the surface mainly by electrostatic attraction. In the present study, the surfactant concentration was below CMC of SDS. Since electrostatic attraction is a prerequisite for the formation of monolayer cluster on the biomass surface, head group adsorption, in turn, influences the extent of hydrophobic tail interaction. Therefore, with increasing pH, a decrease in OSO_3^- electrostatic attraction with negatively charged surface diminishes the opportunities for intermolecular hydrophobic stabilization at the solid/liquid interface resulting in greatly diminished sorption when pH exceeds the point of zero charge (pzc) of cone biomass. Basically, the negative charge on cone biomass increased with increasing pH which was reported by Ucun et al. [14]. It has also reported that zeta potential and surface charges values that the cone biomass is negatively charged in a wide pH range (3.3 -8.8) [14]. A similar behaviour was observed for SDS adsorption on hematite [23], on rice husk [5], and on modified alumina [4].

3.3. Effect of adsorbent (pine cone) dosage on SDS kinetic adsorption

Amount of adsorbent or adsorbent dosage represents an important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of the adsorbate. It was found from Fig. 6 that the increase in pine cone biomass dosage from 0.020 to 0.04 g resulted in decrease in the amount of adsorbed SDS from 71.54 to 26.55 mg g^{-1}. The decrease in amount of SDS adsorbed, q_e (mg g^{-1}) with increasing pine cone biomass is because of the split in the flux or the concentration gradient between the solute concentration in the solution and the solute concentration in the surface of the adsorbent [13,24]. Thus with increasing adsorbent mass, the amount of SDS adsorbed onto unit weight of the pine cone biomass gets reduced, thus causing a decrease in q_e value with increasing adsorbent mass concentration. Although the number of adsorbent sites per unit mass of a adsorbent should remain constant, independent of the total adsorbent mass, increasing

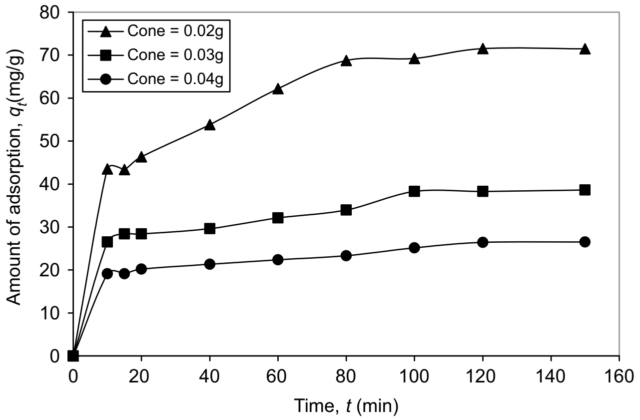

Fig. 6. Effect of adsorbent dosages on the amount of SDS adsorption by pine cone biomass. Volume of SDS solution = 75 ml; initial SDS concentration = 50 ppm; pH = 5.36; temperature = 20°C; shaker speed = 125 rpm.

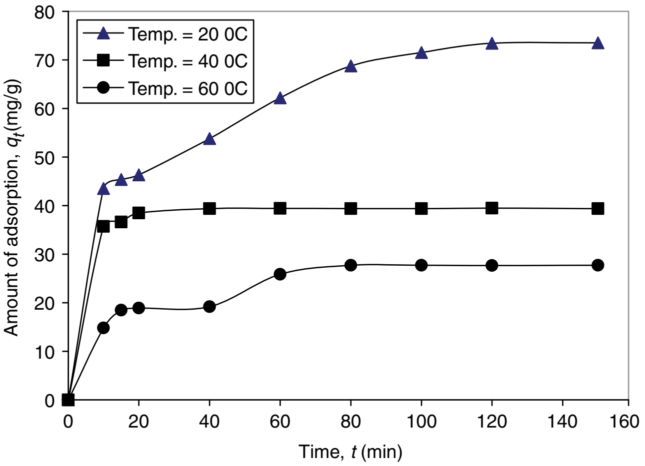

Fig. 7. Effect of temperature on the adsorption of SDS onto pine cone powder: mass of adsorbent = 20 mg; volume of surfactant solution = 75 ml; initial SDS concentration = 50 ppm; pH = 5.36; shaker speed = 125 rpm.

the adsorbent amount in a fixed volume reduces the number of available sites as the effective surface area is likely to decrease [13,25].

In general, pH of final solution increases gradually with the increase in adsorbent dosages [13]. There was increase in the final solution pH (0.4 to 1.1) during adsorbent dose experiments. It may be attributed to evident increase of the amount of negatively charged sites which can induce more H$^+$ ions adsorb on pine cone surface and results in an increase in pH of the final solution.

3.4. *Effect of temperature on dye adsorption kinetics and thermodynamic studies*

The effect of solution temperature on adsorption is generally an important indicator to describe the type of adsorption. The decrease in adsorption with increasing temperature may be indication of physical adsorption and the reverse is generally true for chemisorption [10]. To observe the effect of temperature on the adsorption capacity, experiments were carried out at three different temperatures of 20°C, 40°C and 60°C for a fixed initial SDS concentration of 50 ppm. It has been found from Fig. 7 that with an increase in temperature adsorption capacity decreases. This is is mainly because of decreased surface activity suggesting that adsorption between SDS and pine cone was an exothermic process. With increasing temperature, the attractive forces between the pine cone biomass surface and SDS are weakened and then sorption decreases. This may be due to a tendency for surfactant molecules to excape from the solid phase of biomass to the liquid phase with an increase in temperature of the solution [26].

The Gibbs free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) changes for this SDS adsorption has been determined by the application of Eqs. (10) and (11) and also with the help of Van't Hoff plots which is not shown here. All three thermodynamic parameters are tabulated in Table 1. In general, the change of standard free energy for physisorption is in a range of –20 to 0 kJ mol^{-1} and for chemisorption varies between –80 and –400 kJ mol^{-1} [20]. The overall ΔG^0 (Table 1) values varies from –2105.8 to 1350.2 kJ mol^{-1} at the temperature range studies. These results corresponds to a spontaneous physical adsorption of SDS, indicating that this system does not gain energy from external resource [20,27]. The increase in ΔG^0 with increase in temperature indicates less efficient adsorption at higher temperature. The negative values of ΔS^0 of pine cone suggest a random decrease at their solid/liquid interface and no significant changes occur in the internal structure of the adsorbents through the adsorption [20]. The negative value of enthalpy change (ΔH^0) indicates the exothermic nature of adsorption. Similar types of temperature effects in the removal of SDS from aqueous solution onto sepiolite has been reported by Ozdemir et al. [10].

Table 1
Thermodynamic parameters for adsorption of SDS at different temperatures

Temperature (K)	ΔG^0 (kJmol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1})
293	–2105.8	–27,421	–0.86.4
313	–377.8	–27,421	–0.86.4
333	1350.2	–27,421	–0.86.4

3.5. Effect of contact time and initial SDS surfactant concentration on adsorption kinetics

The initial surfactant concentration has a pronounced effect on its removal from aqueous solutions. The effect of contact time on the adsorption of SDS surfactant was investigated at two different initial concentration onto pine cone adsorbent and results are presented in Fig. 8. It was found that the amount of adsorption i.e., mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial SDS concentrations and equilibrium is attained within 100 min. This relatively short equilibrium time indicates that adsorption is indeed governed by physical interaction [10]. It was also found that the removal of SDS increased from 39.35% to 80.54% with decreasing initial concentration of SDS surfactant from 50 to 20 ppm for which plot is not presented here. Basically, from both the figures, the adsorption percentage decreases and the extent of adsorption increases with increasing initial surfactant concentration. With increasing surfactant concentration leads to the formation of monolayer or bi-layer patches at the surface where sorbate–sorbate associations contribute to increased adsorption [28]. This is also because the initial SDS concentration provides the driving force to overcome the resistance to the mass transfer of surfactant between the aqueous and the solid phase. For constant dosage of adsorbent, at higher initial surfactant concentration, the available adsorption sites of adsorbent become fewer and hence the removal of SDS depends upon the initial concentration [29]. The increase in initial concentration also enhances the interaction between adsorbent and surfactant. Therefore, an increase in initial surfactant concentration leads to increase in the adsorption uptake of SDS. It is also found from the Fig. 8 that the removal of surfactant SDS by adsorption on pine cone is very fast at the initial period of contact but slowed down with time. This kinetic experiment clearly indicated that adsorption of SDS on pine cone is a more or less two step process: a very rapid adsorption of SDS to the external surface followed by possible slow intraparticle diffusion in the interior of the adsorbent. The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy [13]. Similar types of SDS concentration effect also reported by various investigators on different adsorbent system [4,10,23].

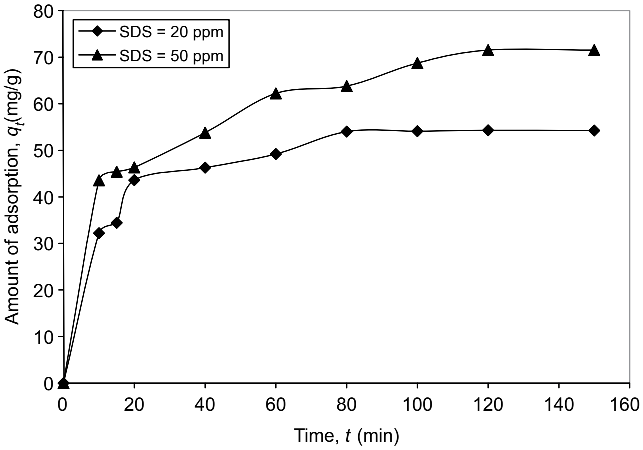

Fig. 8. Effect of contact time and initial SDS concentration on the amount of adsorption (removal) of SDS onto pine cone powder: mass of adsorbent = 20 mg; volume of SDS solution = 75 ml; pH = 5.36; temperature = 20°C; shaker speed = 125 rpm.

3.5.1. Adsorption kinetics

The prediction of batch adsorption kinetics is necessary for the design of industrial adsorption columns. The nature of the adsorption process will depend on physical or chemical characteristics of the adsorbent system and also on the system conditions. In the present study, the applicability of the pseudo-first-order (Eq. (5)) and pseudo-second-order model (Eqs. (6)–(8)) was tested for the adsorption of SDS onto pine cone biomass particles. Both these models has been fitted with experimental data at various physicochemical conditions for which all fitting plots are not presented here. As per Lagergren pseudo-first-order model, a plot of $\log(q_e - q_t)$ versus t gives a straight line with poor linear regression coefficient (R^2) in the range of 0.76 to 0.95 at different adsorbent dosages (Fig. 9). The same pseudo-first-order model was fitted with kinetic adsorption experimental results in case of initial solution pH effect, initial SDs concentration effect and system temperature respectively but it gives very poor linear regression coefficient, R^2 value which are not presented here. Moreover, pseudo-first-order kinetic model predicted a significantly lower value of the equilibrium adsorption

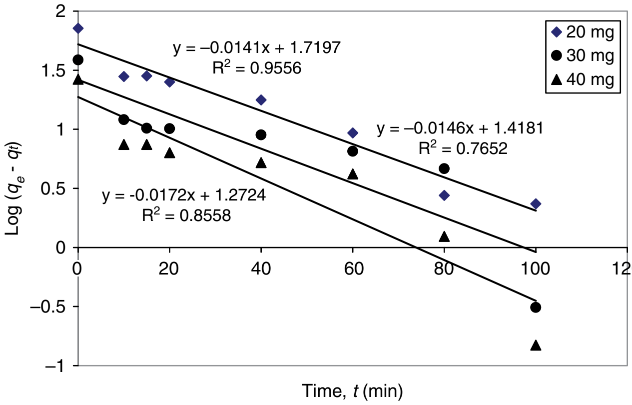

Fig. 9. Pseudo-first-order kinetic model for SDS adsorption by pine cone at different adsorbent dosages.

capacity (q_e) than the experimental value, which is not also shown here but indicates the inapplicability of this model. The adsorption data were then analysed using the pseudo-second-order kinetic model. The plot t/q_t versus t should give a straight line with higher linear correlation coefficients if pseudo-second-order kinetics is applicable and q_e, k_2 and h can be determined from the slope and intercept of the plot respectively. All kinetic parameters including linear correlation coefficient (R^2) obtained from fitting model plots with experimental data under different conditions were presented in Table 2. Higher linear regression coefficients (R^2) (Table 2) with respect to fitted pseudo-first-order model suggest that adsorption of SDS surfactant on pine cone biomass follows pseudo second-order kinetics. Moreover, calculated, $q_{e\ cal}$ values from pseudo-second-order fitting model (Table 2) is very close to the experimental q_e values (Table 2) also suggest the suitability of this model. Also from Table 2 the adsorption capacity increases with increase in initial surfactant concentration but decreases within initial solution pH, amount of adsorbent, and temperature respectively. Whereas the values of rate constant, k_2 decrease with initial surfactant concentration for pine cone biomass. The reason for this behaviour may be due to the lower competition for the sorption sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. The overall rate constant, k_2 increased as the adsorbent dosage increased and also initial adsorption rate, h varied with the variation in the adsorbent dosage (Table 2). Similar type kinetic model parameters were obtained by various researchers for a few other observations systems reported in the literature [7,20,24,30–32].

The half-adsorption time of the surfactant, $t_{1/2}$ i.e., the time required for the pine cone to uptake half of the amount adsorbed at equilibrium, is often considered as a measure of the rate of adsorption and for the second-order process is given by the relationship [31]:

$$t_{\frac{1}{2}} = \frac{1}{k_2 q_e} \tag{12}$$

The calculated values of $t_{1/2}$ for the SDS adsorption by pine cone are 6.28 s (0.104 min) and 9.178 s (0.1529 min) for an initial concentration range of 20, 50 ppm respectively. Similarly for other process variables, half adsorption time ($t_{1/2}$) can also be calculated which are not presented here.

3.6. Intraparticle diffusion and adsorption mechanism

For the process design and control of adsorption systems, it is important to understand the underlying mechanism that results in the apparent dynamic behaviour of the system. The removal of SDS by adsorption on pine cone biomass was very rapid at the initial period of contact time and then become slow and stagnates

Table 2
Pseudo-second-order kinetic parameters for SDS adsorption on pine cone

System parameters	q_e (mg/g), experimental	k_2 [(g mg^{-1}) min]	q_e (mg g^{-1}), calculated	h [(mg g^{-1}) min]	R^2
Adsorbent dosage (mg)					
20	71.50	0.00145	75.18	8.250	0.9924
30	38.60	0.00346	39.68	5.457	0.990
40	26.55	0.0058	26.95	4.21	0.992
Initial SDS concentration (ppm)					
20	54.27	0.00280	56.81	9.055	0.996
50	71.54	0.00146	74.62	8.181	0.992
pH					
4.28	105.20	0.0111	105.26	123.45	0.999
5.36	39.35	0.00298	39.52	4.66	0.988
7.49	29.93	0.0022	33.44	2.563	0.969
Temperature					
30°C	45.07	0.0063	45.66	13.11	0.9996
45°C	39.53	0.0087	39.84	13.79	0.9998
60°C	39.11	0.0047	39.22	7.16	0.9988

with time. For a solid/liquid sorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both. The mechanism of SDS removal from aqueous phase by adsorption is assumed to consist of following four steps [20,24,33]:

a. Migration of the SDS molecules from the bulk solution to the surface of the sorbent.
b. Diffusion of SDS through the boundary layer to the surface of the sorbent.
c. Adsorption of SDS at an active site on the surface of the sorbent.
d. Intraparticle diffusion of SDS into the interior of the sorbent.

The overall rate of sorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. Whatever the case, external diffusion will be involved in the sorption process. The sorption of SDS onto pine cone particles may be controlled due to film diffusion at earlier stages and as the adsorbent particles are loaded with SDS anions, the sorption process may be controlled due to intraparticle diffusion.

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot (Eq. (9)). The plot of amount sorbed per unit weight of sorbent, q_t (mg g^{-1}) versus square root of time, $\sqrt{t}$ is shown in Fig. 10 for initial SDS concentration. Intraparticle diffusion plots for different solution pH change, adsorbent dosages, different temperatures are give same trend which are not presented here.

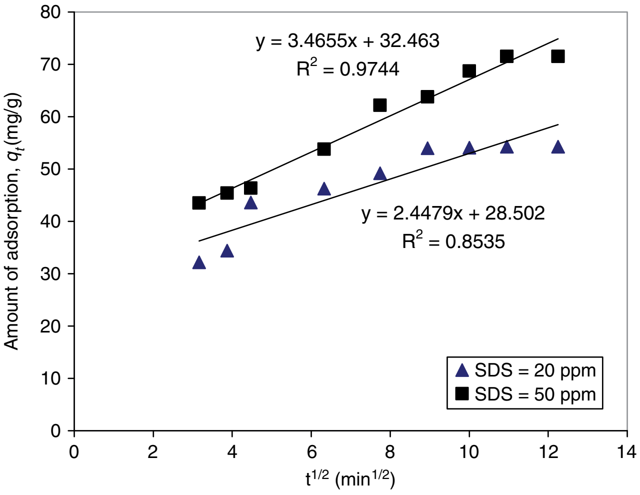

Fig. 10. Intraparticle diffusion model on different initial SDS concentrations.

Fig. 10 shows that the adsorption plots are not linear over the whole time range and can be separated into two linear regions which confirm the multi stages of adsorption. The dual nature of the curve (Fig. 10) was obtained due to the varying extent of adsorption in the initial and final stages of adsorption experiment. This plot represented the two different stages viz. external mass transfer followed by intra-particle diffusion, signified that the SDS molecules were transported to the external surface of the pine cone particle through film diffusion and its rate was very fast. After that, SDS molecules were entered into pine cone particles by intra-particle diffusion through pores. Generally, when adsorption steps are not dependent of one another, the plot of q_t against $t^{0.5}$ should give two or more intercepting lines depending on the actual mechanism [34]. Moreover from Fig. 10, conclusion can be made that none of plot give linear straight line segment passing through the origin, $I \neq 0$ which is not shown here. This deviation from the origin may perhaps be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. This indicated that there is some degree of boundary layer external control and this further showed that intraparticle diffusion was not only the rate-limiting step, but also be the rate controlling of sorption or all may be operating simultaneously [35].

The diffusion coefficient, D, largely depends on the surface properties of adsorbents. The diffusion coefficient for the intra-particle transport of different initial concentrations of SDS were also calculated using the following relationship [7]:

$$t_{1/2} = 0.03 r_0^2 / D \tag{13}$$

where $t_{1/2}$ is the half life in seconds as calculated from Eq. (13), r_0 the radius of the adsorbent particle in centimetres and D is the diffusion coefficient value in cm^2 s^{-1}. Here surface weighted mean diameter of pine cone particles of 27.25 μm (radius = 13.62 μm = 13.62 × 0.0001 cm = 0.001362 cm) has been utilised. The diffusion coefficients, D values were found to be 8.86×10^{-9} cm^2 s^{-1} and 6.063×10^{-9} cm^2 s^{-1} for an initial SDS concentration of 20, and 50 ppm respectively which is increases with change in initial SDS concentration.

3.6.1. Adsorption equilibrium isotherm

Analysis of adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. Fig. 11 gives results on Freundlich isotherm fittings for pine cone with linear correlation coefficient (R^2) of 0.995. Freundlich constants i.e., adsorption capacity, K_f and rate of adsorption, n, are calculated from this plot which are 25.0 mg g^{-1} and 3.18 respectively. The value

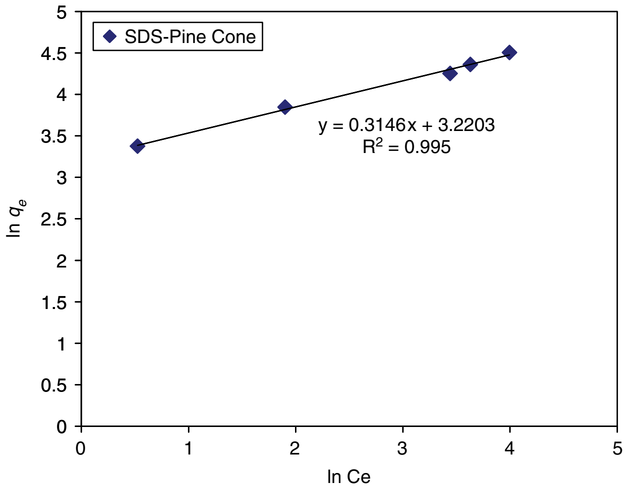

Fig. 11. Freundlich plot: amount of adsorbent (pine cone) added = 20 mg; initial SDS concentration = 10, 20, 50, 60, 80 ppm; pH = 7.21; temperature = 20°C; shaker speed = 120 rpm.

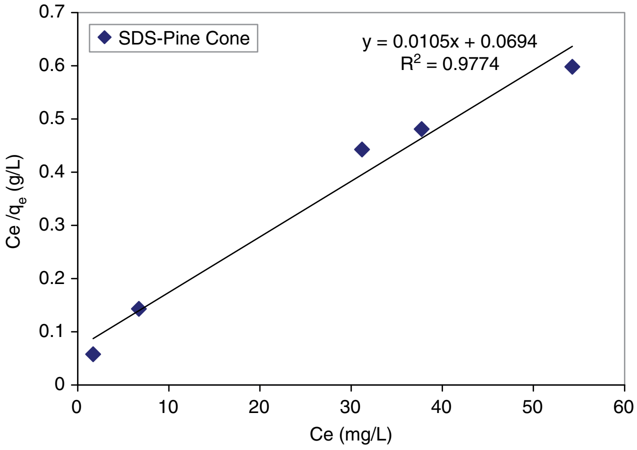

Fig. 12. Langmuir plot: amount of adsorbent (pine cone) added = 20 mg; initial SDS concentration = 10, 20, 50, 60, 80 ppm; pH = 7.21; temperature = 20°C; shaker speed = 120 rpm.

of "*n*" is larger than 1 which indicates the favourable nature of adsorption and a physical process [8,27].

Fig. 12 gives results on Langmuir-1 isotherm fittings for pine cone biomass adsorbent. The maximum monolayer adsorption capacity of pine cone, q_m, and constant related to the binding energy of the sorption system, K_a is calculated from plot 12 which are 95.23 mg g^{-1} and 0.15130 respectively for SDS-pine cone system.

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by [36]:

$$R_L = \frac{1}{1 + K_a C_0} \tag{14}$$

where K_a is the Langmuir constant and C_0 is the initial SDS concentration (mg l^{-1}). The quantity (R_L) is taken to the relative volatility in vapour–liquid equilibrium. It is easy to verify that for a favourable system, R_L lies between 0 and 1, for each of the different initial concentrations of SDS, it's larger than zero for an unfavourable system [37].

The separation factor, R_L has been calculated from Langmuir plot. It has been found that the calculated R_L values are 0.3979, 0.2483, 0.1321, 0.0992 and 0.0763 at initial dye concentration of 10, 20, 50, 60, 80 ppm respectively. These R_L values indicates favorable adsorption as it lie in $< 0 < R_L < 1$. From Figs. 11 and 12, it is also found that the adsorption equilibrium data fit both Freundlich and Langmuir equations with a correlation coefficient value of 0.995 and 0.977 respectively. The best fit of equilibrium data in the Freundlich isotherm model confirms the heterogeneous coverage of SDS onto pine cone particles.

3.6.2. Design of single-stage batch adsorber from isotherm data

Adsorption isotherms can be used to predict the design of single batch adsorption system [13,35]. The schematic diagram for a single-stage batch adsorber was found to be similar to the used in the removal of methylene blue (MB) dye by pine cone biomass [13]. Freundlich adsorption isotherm data has been utilised to design a single-stage batch adsorption system as per method developed by Kumar et al. [35]. Due to lack of extensive experimental data, empirical design procedures based on adsorption isotherm studies are the most common method to predict the adsorber size and performance. The design objective was to reduce initial SDS concentration of C_0 to C_t (mg l^{-1}) for which total solution is V (L). The amount of added adsorbent was m and the solute loading changes from q_0 (mg g^{-1}) to q_t (mg g^{-1}). Now the SDS concentration on solid changes from $q_0 = 0$ to q_t due to added adsorbent into the system. The mass balance for the SDS in the single stage operation under equilibrium is given by:

$$V\left(C_0 - C_e\right) = m\left(q_e - q_0\right) = mq_e \tag{15}$$

From isotherm experiments, it was found that equilibrium data for SDS on pine cone biomass is better fitted with Freundlich isotherm model and therefore Eq. (15) can be written and rearranged after putting the value of q_e as:

$$\frac{m}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{K_f C_e^{1/n}} \tag{16}$$

Fig. 13 shows a series of plots derived from Eq. (16) between the predicted amount of pine cone particles

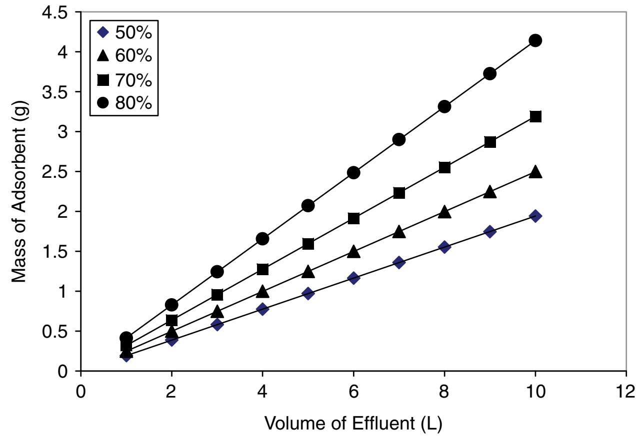

Fig. 13. Adsorbent mass (m) against volume of solution treated (l).

required to remove SDS of initial concentrations of 20 ppm for 50%, 60%, 70% and 80% SDS removal at different solution volumes (1–10 l) for a single-stage batch adsorption system, for which the design procedure is outlined.

4. Conclusions

The present study shows that the scales of cone biomass of pure *Pinus radiate,* an agricultural by-product waste can be used as an effective alternative low cost adsorbent for the removal of anionic surfactant, SDS from aqueous solutions. The amount of SDS uptake on pine cone biomass was found to increases with an increase in initial SDS concentration, contact time, but was found to decrease with increase in solution pH, amount of adsorbent, and system temperature. It was observed that the adsorption was pH dependent and the maximum adsorption of 105.19 mg g^{-1} occurred at pH of 4.28 for an initial SDS concentration of 50 ppm. Kinetic experiments clearly indicated that adsorption of SDS on pine cone biomass is a two step process: a rapid adsorption of SDS onto the external surface followed by intraparticle diffusion into the interior of adsorbent which has also been confirmed by intraparticle diffusion model. Overall, the kinetic studies showed that the SDS adsorption process followed pseudo-second-order kinetics models. The Langmuir and Freundlich both adsorption isotherms were demonstrated to provide best correlation for the adsorption of SDS onto pine cone biomass. The maximum monolayer adsorption capacity of pine cone biomass was found to be 95.23 mg g^{-1}. The constant value, R_L (low separation factor) in Langmuir isotherm and Freundlich constant, n, both give an indication of favorable adsorption. The thermodynamic analysis indicates that system is spontaneous, exothermic and physical processes in nature.

Acknowledgements

Chemical Engineering Department of Curtin University, Perth for financial support through internal funding project entitled “Metal Ion Adsorption”; Professor De-Yu Li of Physics department for help in taking XRD; Ann Carroll of Chemical Department for laboratory helping and Zhezi Zhang for FTIR analysis.

Symbols

C_f — final SDS concentration, ppm (mg l^{-1})
C_0 — initial SDS concentration, ppm (mg l^{-1})
C_t — SDS concentration at time t, ppm (mg l^{-1})
D — diffusion coefficient ($cm^2 s^{-1}$)
ΔG^0 — Gibbs free energy change (kJ mol^{-1})
ΔH^0 — enthalpy change (kJ mol^{-1})
ΔS^0 — entropy change (J K^{-1} mol^{-1})
k_1 — pseudo-first-order rate constant (min^{-1})
k_2 — pseudo-second-order rate constant [(mg g^{-1}) min]
K_f — Freundlich adsorption constant (mg g^{-1})
K_{id} — intra-particle rate constant [(mg g^{-1}) $min^{0.5}$]
M — mass of adsorbent per unit volume (gl^{-1})
m — amount of adsorbent added (g)
n — Freundlich constant
q — amount of adsorbate per gram of adsorbent (mg g^{-1})
q_e — amount of adsorbate per gram of adsorbent at equilibrium (mg g^{-1})
q_t — amount of adsorbate per gram of adsorbent at any time, t
q_m — equilibrium adsorption capacity using model
q_{max} — maximum adsorption capacity (mg g^{-1})
R^2 — linear regression coefficient
R_L — separation factor
r_0 — radius of adsorbent particle (cm)
t — time (min)
T — temperature (K)

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