

CHAPTER III

LITERATURE REVIEWS

3.1 Adsorption by living/dead microbial biomass

The uptake or accumulation of chemicals by microbial mass has been termed biosorption (Tsezos and Bell, 1989; Hu, 1992; Kumar et al., 1998). Dead bacteria, yeast, and fungi have all been used for the purpose of decoloring dye effluents. Textile dyes vary greatly in their chemistries, and therefore their interactions with micro-organisms depend on the chemistry of a particular dye and the specific chemistry of the microbial mass (Polman and Brekenridge, 1996). Depending on the dye and the species of organism, different binding rates and capacities will be observed. Both living and dead biomass can be used to remove hazardous organics, but maintaining a viable biomass during adsorption is difficult, because it requires a continuous supply of nutrients and avoidance of organic toxicity to the micro organisms. The use of dead cell in biosorption is more advantage for water treatment in that: dead organisms are not affected by toxic wastes and they do not require a continuous feed of nutrients.

3.2 *Caulerpa lentillifera*

Caulerpa lentillifera (Figure 3.1) is a green macroalga classified in:

Phylum: Protista

Division: Chlorophyta (Green algae group)

Class: Chlorophyceae

Order: Caulerpales

Family: Caulerpaceae

Genus: *Caulerpa*

Species: *Caulerpa lentillifera*

This seaweed commonly grows rapidly in rainfed agricultural areas, thus becomes unwanted material. It can tolerate a salinity range of 30-35 ppt. The characteristics of this alga are siphonous form with septum cover cell to produce gaemetangium in reproducing period. Generally *Caulerpa lentillifera* is found growing on rocks, and sand at shallow water near coral. The branch height, looked

just like a bunch of pepper, is 1-6 cm which consists of small green ramulous, spherical in shape with a diameter of around 1.5 – 2 mm.

The green macro algae *Caulerpa lentillifera* is one of the edible algae in some Asian countries such as Malaysia, Singapore, Philippines, and Thailand. Other than this purpose, the alga has been grown in Thailand because of its ability for the treatment of wastewater in the shrimp farm which contains high nitrogen concentration. However, its rapid growth requires the farmer to regularly remove and dispose of the overgrown alga. Previous work indicated that this alga, unwanted agricultural material, could well be employed as an effective biosorbent for heavy metals (Sungkhum, 2003).

3.3 Mechanism of biosorption

The kinetics of adsorbate uptake by green algae can be described as a two step mechanism.

1. The first step is the passive transport mechanism, which is fast (less than 5-10 minutes), reversible and metabolism-independent surface reaction called “biosorption” such as physical sorption or ion-exchange of the sorbate species at the cell surface.
2. The second step is the active transport mechanism, which involves the uptake of the adsorbates into the living or dead cells; a slower binding process, irreversible and metabolism-dependence called “bioaccumulation”

Bacteria, cyanobacteria, algae, fungi, and yeast are able to remove pollutants from their surrounding environment by both mechanisms. Metabolism-independent adsorption of adsorbate to cell wall (biosorption) which is polysaccharides or other materials occurs in living and non-living cells and is generally rapid. Metabolism-dependent intracellular uptake or transport occurs in living cell (bioaccumulation) usually at a much slower rate than adsorption, although in longer run greater amount of adsorbate may be accumulated by this mechanism.

3.4 Equilibrium behavior and sorption isotherms

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of biosorption systems used for the removal of organic pollutants. The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherm models are the most frequently used models in the literatures describing the non-linear

equilibrium between adsorbed organic on the cells (q_e) and the organic pollutant in the solution (C_e) at a constant temperature.

The Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites is given by Eq. (3.1).

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3.1)$$

where parameter q_m and b are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time. The Langmuir equation is used for homogeneous surfaces. The Freundlich isotherm model assumes neither homogeneous nor limited level of adsorption. The Freundlich equation has the general form:

$$q_e = K_F C_e^{1/n} \quad (3.2)$$

where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Freundlich, 1906). Eqs. (3.1) and (3.2) can be linearized in logarithmic form as shown below.

Linear form of Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{b q_m}\right) \left(\frac{1}{C_e}\right) \quad (3.3)$$

Linear form of Freundlich equation:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (3.4)$$

Langmuir and Freundlich constants, i.e., q_m , b , $1/n$ and K_F , were calculated from the slope and interception of the linear plots.

3.5 Adsorption kinetics in batch systems

If the movement of organic pollutant molecule from the bulk liquid to the liquid film or boundary layer surrounding the biosorbent is ignored, the following sequence steps can take place in the biosorption process of porous biosorbent: transport of solute molecules from the boundary film to the external surface of biosorbent (film diffusion), transfer of molecules from the surface of biosorbent to the intraparticle active sites and uptake of molecules by the active site of sorbent. In the removal of

organic from wastewater, it is important for designed purposes to investigate the mechanisms of adsorption and potential rate controlling steps which control the adsorption rate. In order to find the contribution of rate controlling steps such as external mass transfer, intraparticle diffusion, and adsorption process, the kinetic models could be used to test the experimental data following the procedure described by Aksu (2005).

In the first step of adsorption, the film diffusion is an important rate-controlling step and the external mass transfer or boundary layer diffusion can be characterized by the initial rate of solute sorption. In this case, adsorption rate is expected to be proportional to the concentration, it means that this step is a first-order process (Chu and Chen, 2002) and can be defined as:

$$\frac{dC}{dt} = k_1 C \quad (3.5)$$

where C is the pollutant concentration in the wastewater and k the first-order reaction rate constant. Eq. (3.5) can be integrated to:

$$\log \frac{C_0}{C} = \frac{1}{2.303} k_1 t \quad (3.6)$$

If intraparticle diffusion is involved in the sorption process, the model developed by Weber and Morris (Weber and Morris, 1963) can be used to find the region where the intraparticle diffusion is rate-limited. In this model, the rate of intraparticle diffusion is a function of $t^{0.5}$ and can be defined as follows:

$$q = f\left(\frac{Dt}{r_p^2}\right)^{0.5} = k_i t^{0.5} \quad (3.7)$$

where r_p is particle radius, D the effective diffusivity of solute within the particle, and k_i the intraparticle diffusion rate. If intraparticle diffusion is rate-limited; then a plot of adsorbate uptake (q) versus the square root of time ($t^{0.5}$) would result in the linear relationship and k_i value can be obtained from this plot.

In many cases, the kinetics of biosorption based on overall adsorption rate by biosorbent is described by the first-order (Lagergren, 1898) and pseudo-second order kinetic models (Ho and McKay, 1999). The first-order expression based on the solid capacity is

$$\frac{dq}{dt} = k_1 (q_e - q) \quad (3.8)$$

where q_e and q are the amount of adsorbed dye on the biosorbent at the equilibrium and at time t , respectively, and k_1 the rate constant of first-order biosorption. After integration and applying the boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q$; the integrated form of Eq. (3.8) becomes

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (3.9)$$

Therefore, a straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model. In order to fit Eq. (3.9) to experimental data, the equilibrium sorption capacity, q_e , must be known in a prior. In many cases q_e is unknown and it is difficult to fit the experimental data to the model. For this reason it is necessary to obtain the real equilibrium sorption capacity by extrapolating the experimental data to $t = \infty$ by using the trail and error method. Furthermore, in most cases the first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 20-30 min of the sorption process.

Another most widely used kinetic expression is the pseudo second-order rate expression derived by Ho and McKay (1999) where sorption capacity was assumed to be proportional to the number of active sites occupied on the sorbent. The pseudo second-kinetic rate law can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (3.10)$$

where k_2 is the rate constant for second-order biosorption. For the boundary condition $t = 0$ to $t = t$ and $q = 0$ to $q = q$; the integrated linear form of Eq. (3.10) becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.11)$$

If the second-order is applicable, the plot of t/q against t in Eq. (3.11) should give a linear relationship, from which k_2 and q_e can be determined from the slop and intercept of the plot. In this case, there is no need to know q_e beforehand. Some literature reviews on the kinetic model of various adsorption systems are shown in Table 3.1.

3.6 Adsorption kinetics in continuous packed bed systems

When the dye containing solution passes through a packed bed column, at the beginning, most of the dye gets adsorbed on biosorbent so the dye concentration in the effluent is either very low or in some cases not detectable. As the biosorption

continues, the dye concentration in the effluent rises, slowly at first, and then abruptly. When this abrupt rise or breakthrough occurs, the flow is stopped. The performance of the continuous packed bed is described through the concept of the breakthrough curve. The time for breakthrough appearance (breakthrough time) and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of the biosorption column.

The general position of the breakthrough curve along the time or volume axis depends on capacity of the column with respect to the feed concentration and flow rate. The breakthrough curve shows the loading behavior of the dye to be removed from solution in a fixed bed and is usually expressed in terms of normalized concentration defined as a ratio of the dye concentration in the effluent to the inlet dye concentration (C/C_0) which is a function of time or volume of effluent (V_{eff}) for a given bed height.

A successful design of a column adsorption process requires a proper prediction of concentration-time profile or breakthrough curve of effluent under given specific operating conditions. Developing model to accurately describe the dynamic behavior of adsorption in a fixed bed system is inherently difficult since the concentration of the adsorbate as the feed moves through the bed are differential in nature and usually required complex numerical methods to solve (Aksu, 2005). However, various simple mathematical models have been developed to predict the dynamic behavior of the column. The models used in the literatures to characterize the fixed bed performance are presented here.

The service time of the continuous flow column can be considered as a function of the bed depth of the algal sorbent. Bed depth service time model (BDST) is a simple model which described the relationship (Faust and Aly, 1987):

$$t_b = \frac{N_0 D}{C_0 V'} - \frac{1}{K_{BDST} C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (3.12)$$

where the column service time was selected as the time when the effluent dye reaches the break point (t_b).

Thomas model (Thomas, 1944) can also be used to characterize the column using the V_{eff} . The model has the following form:

$$\frac{C}{C_0} = \frac{1}{1 + \exp(k_{TH} / Q(q_{TH}X - C_0V_{eff}))} \quad (3.13)$$

where k_{TH} is the Thomas rate constant, q_{TH} the maximum solid-phase concentration of the solute, Q the flow rate, and X the amount of the sorbent in the column. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{TH}q_{TH}X}{Q} - \frac{k_{TH}C_0}{Q}V_{eff} \quad (3.14)$$

The kinetic coefficient k_{TH} and the adsorption capacity of the bed q_{TH} can be determined from the plot of $\ln\left(\frac{C}{C_0} - 1\right)$ against t at a given flow rate.

3.7 Controlling factors for removal of basic dyes

Basic dye biosorption is influenced by a number of various factors as described below.

3.7.1 pH

The pH value of the solution is an important parameter in the adsorption process. The optimal pH for the adsorption system strongly depends on the dye and adsorbent surface chemistries. Normally, there exists an optimum pH for a maximum uptake for each adsorption system. The difference in adsorption capacity at different pH value results from:

- The competition between cationic dyes and protons for the binding site at low pH.
- The change in functional groups on the cell wall.

In most cases, the adsorption of cationic dye should decrease at a lower pH. This may be due to the occurrence of positive charge on the surface of an adsorbent in an acidic medium. Examples of the findings on the effects of pH are given in Table 3.2.

3.7.2 Initial dye concentration

The studies on the effects of initial dye concentration have been done on various adsorption systems. The adsorption capacity often was found to increase with an increase in initial dye concentration, and these are summarized in Table 3.3.

3.7.3 Adsorbent dosage

The increase in the amount of adsorbent increases the adsorbent surface area and availability of adsorption sites. Although the adsorption increases by increasing the adsorbent dosage, the amount of dye adsorbed per unit mass of adsorbent was often found to decrease. Some literature reviews on the effects of adsorbent dosage are shown in Table 3.4.

3.7.4 Adsorbent particle size

The smaller particle size of adsorbent provides larger surface area on the adsorbent. The finer granular or powder usually enhances the adsorption capacity or shortens the equilibrium time of the adsorption processes. Past researches on the effects of particle size are shown in Table 3.5.

3.7.5 Temperature

The increase/decrease in temperature is seen to influence the biosorption capacity. For chemisorption mechanism, the rise in temperature increases in number of molecules acquiring sufficient energy to undergo chemical reaction (endothermic reaction). However, the extremely high temperature can lead to the destruction of cell surface which can alter the binding site on the alga surface. Being an exothermic reaction, on the other hand, the adsorption capacity can be enhanced by decreasing temperature. Different adsorption mechanisms have been investigated as shown in Table 3.6.

3.8 Adsorption thermodynamics

Standard Gibbs free energy (G°), standard enthalpy (H°) and entropy (S°) changes for the adsorption process can be calculated from Eqs. (3.15)–(3.17) by using the results from isotherm studies:

$$\ln\left(\frac{1}{b}\right) = \frac{\Delta G^\circ}{RT} \quad (3.15)$$

$$\ln b = \ln b^\circ - \frac{\Delta H^\circ}{RT} \quad (3.16)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3.17)$$

where b is the Langmuir constant that is related with the energy of adsorption, b° a constant, R the ideal gas constant, and T the temperature. The meaning of the

calculated thermodynamic parameters can be summarized in Table 3.7 and the thermodynamic parameters investigated in the past researches are tabulated in Table 3.8.

3.9 Desorption

Different processes have been used in various studies to desorb the dye molecules from biomass, e.g.

- Using high concentration of H^+ ions (acid treatment) (Namasivayam and Sumithra, 2005)
- Eluting by basic solution (alkali treatment) (Gupta et al., 2005)
- Washing with warm/hot water (heat treatment) (Inthorn et al., 2004).

Past researches showed the applicability of these methods. The choice of choosing desorption method mainly depends on the interaction between the adsorbate and adsorbent. Although desorption is valuable for the recovery of metals, the dye recovery is sometimes not economically practicable, especially when using very cheap adsorbent. Moreover, the recovered dyes are not easily purified. In this case, the used adsorbent is better to be disposed off as a solid waste than to be desorbed which could end up with the generation of more hazardous wastewater.

3.10 Concluding remarks

The investigation of adsorption characteristics, isotherms, kinetics, and thermodynamics is useful for the determination of adsorption mechanism. The attraction between the dye molecules and the adsorbent surface can be physical (physisorption) or chemical (chemisorption). For physisorption, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface. The multilayer cover is also possible in this case. The adsorbate molecules can be desorbed easily by washing with hot water. In contrast, chemisorption occurs when the adsorbates form stronger bonds with the adsorbent surface, implying monolayer coverage.

The adsorbent surface chemistry gives the information on the type of chemical bond between the adsorbent and the dye molecules. The charge functional groups on the adsorbent surface can imply the electrostatic interaction (Al-Ghouti et al., 2003). The ion-exchange process can also be stated when the adsorbate displace other ions on the adsorbent surface.

Table 3.1 Literature reviews on the kinetic model of various adsorption systems

Adsorbent/dyes	Kinetic model	References
Coir pith/ rhodamine B	First order	Namasivayam et al., 2001
Aspergillus niger/ Congo red	First order	Fu and Viraraghavan, 2002
Giant duckweed/ Methylene blue	First order	Waranusantikul et al., 2003
Indian Rosewood Sawdust/ Methylene blue	First order	Garg et al., 2004
Neem leaf powder/ Methylene blue	First order	Bhattacharyya and Sharma, 2005
Wood/Basic blue 69	Pseudo-second order	Ho and McKay, 1998a
Peat/Basic blue 69	Pseudo-second order	Ho and McKay, 1998b
Sphagnum moss peat/ Basic blue 3	Pseudo-second order	Ho and McKay, 1998c
Sphagnum moss peat/Basic blue 69	Pseudo-second order	Ho and McKay, 1998c
Pith/ Basic red 22	Pseudo-second order	Ho and McKay, 1999
Aspergillus niger/ Basic blue 9	Pseudo-second order	Fu and Viraraghavan, 2000
Activated Clay/Basic red 18	Pseudo-second order	Ho et al., 2001
Date pits/ Methylene blue	Pseudo-second order	Banat et al., 2003
<i>Enteromorpha prolifera</i> / Acid red 274	Pseudo-second order	Ozer et al., 2005
<i>Pithophora sp.</i> / Malachite green	Pseudo-second order	Kumar et al., 2005
<i>Rhizopus arrhizus</i> / Gemazol Turquoise blue G	Pseudo-second order	Aksu and Çağatay, 2006

Table 3.2 Effects of pH on various adsorption systems

Adsorption system	Concluding results	References
<i>Aspergillus niger</i> / Congo red	The maximum dye adsorption occurred at pH of 6.0.	Fu and Virarathavan, 2000
Coir pith/ Rhodamine-B	The percent removal increased with increasing pH.	Namasivayam et al., 2001
Date pits/ Methylene blue	The uptake of methylene blue was low under the acidic condition.	Banat et al., 2003
Giant duckweed/ Methylene blue	The percentage sorption of methylene blue was minimum at the initial pH of 2, then increased and remained nearly constant over the pH ranges of 3-11.	Waranusantikul et al., 2003
Indian Rosewood sawdust/ Methylene blue	The dye adsorption efficiency was not affected by pH except minor variations.	Garg et al., 2004
Neem leaf powder/ Methylene blue	The pH of the medium did not show any significant effect on the uptake of methylene blue.	Bhattacharyya and Sharma, 2005
<i>Pithophora sp.</i> / Malachite green	It was observed that the amount of dye adsorbed varies with pH. The q_e value increased with increasing pH from 2 to 5. With further increase in pH, the amount of dye adsorbed decreased slowly. The maximum amount of dye (887.5 mg g ⁻¹) was adsorbed at a pH of 5.	Kumar et al., 2005
<i>Azolla filiculoides</i> / Acid blue 15	The Langmuir model parameters were largely dependent on the initial solution pH values. Both the maximum dye uptake q_m and the Langmuir equilibrium constant b increase with increase in initial pH from 4 to 7.	Padmesh et al., 2006
Yellow passion fruit waste/	The removal of MB increased	Pavan et al., 2007

Methylene blue

significantly with increases in the pH solutions ranging from 2 up to 7. For pH values higher than 7 and lower than 10, the amount of dye removal was kept practically constant.

Table 3.3 Effects of initial dye concentration on various adsorption systems

Adsorption system	Concluding results	References
Coir pith/ Rhodamine-B	The uptake of dye increased with an increase in dye concentration and remained nearly constant after equilibrium time.	Namasivayam et al., 2001
Diatomaceous clay/ Methylene blue	The amount of methylene blue adsorbed increased with an increase in methylene blue concentration.	Shawabkeh and Tutunji, 2003
Sawdust/ Methylene blue	Percent adsorption efficiency of sawdust decreased with an increase in initial dye concentration in the solution. Although the percent adsorption decreased with an increase in initial dye concentration, the actual amount of dye adsorbed per unit mass of adsorbent increased with an increase in dye concentration in the test solution.	Garg et al., 2004
Neem leaf powder/ Methylene blue	The amount adsorbed increased with an increase in the dye concentration.	Bhattacharyya and Sharma, 2005
Sugar beet pulp/ Gemazol turquoise blue-G	Increasing initial dye concentration increased the number of interactions between dye anions and sorbent, which enhanced the sorption process. Hence, a higher initial concentration of Gemazol turquoise blue-G increased the biosorption rate.	Aksu and Isoglu, 2006

Table 3.4 Effects of adsorbent dosage on various adsorption systems

Adsorption system	Concluding results	References
Water hyacinth roots/ Methylene blue	The results followed the predicted pattern of increasing percentage sorption as the dosage was increased. The removal of methylene blue increased from 4.8 to 98% when the dosage changed from 0.1 to 0.5 g at room temperature.	Low et al., 1995
Date pits/ Methylene blue	Although the uptake of methylene blue decreased with an increase in adsorbent dosage, the residue concentration of methylene blue in solution decreased. Further increase in adsorbent dosage above 5 mg ml ⁻¹ had no effect on percentage removal of methylene blue.	Banat et al., 2003
Giant duckweed/ Methylene blue	The percentage of dye removal increased with the increasing amount of biomass, however the ratio of dye sorbed to biomass (mg g ⁻¹) decreased with the increasing amount of biomass.	Waranusantikul et al., 2003
Sawdust/ Methylene blue	The percent adsorption increased and equilibrium time decreased with adsorbent dose. The increase adsorbent could be attributed to increased adsorbent surface area and availability of more adsorbent sites. But the unit adsorption decreased with adsorbent dose.	Garg et al., 2004
De-oil soya/ Quinoline yellow	The uptake of the dye increased with increased amount of adsorbent from 0.05 to 0.20 g at each temperature. Further increase in the amount of adsorbent did not affect the	Gupta et al., 2005

Guava leaf powder/ Methylene blue	uptake capacity significantly. An increase in adsorbent dosage increased available surface area and active sites. At a dosage of 2 g/dm ³ maximum percentage removal was obtained. At the same time amount of dye adsorbed per unit mass of adsorbent decreased with increase in adsorbent dosage.	Ponnusami et al., 2007
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Table 3.5 Effects of adsorbent particle size on various adsorption systems

Adsorption system	Concluding results	References
Diatomaceous earth/ Methylene blue	The dye uptake increased with a finer adsorbent size but only marginal effect.	Al-Ghouti et al., 2003
Waste carbon slurries/ Basic Red	The time required for 50% of the total adsorption decreased with the smaller size adsorbent.	Gupta et al., 2003
Date pits/ Methylene blue	Uptake of methylene blue increased with a decrease in particle size, mainly due to a larger surface area.	Banat et al., 2003
Powder peanut hull/ Fast green FCF	Smaller particles provided more specific area and it was expected that percentage removal would therefore increase. This relationship indicated that powdered adsorbent would be advantageous over granular particles.	Gong et al., 2005
Pine sawdust/ Metal complex dyes	A decrease in the particle size led to an increase in surface area which amplified the adsorption opportunity at the outer space of the pine sawdust.	Özacar and Şengil, 2005
Guava leaf powder/ Methylene blue	The ratios of dyes sorbed increased as the sorbent particle size decreased, but the ratios of dyes sorbed approached the maximum values when the sorbent particle size went above 80-100 mesh.	Ponnusami et al., 2007

Table 3.6 Effect of temperature on various adsorption systems

Adsorption mechanism	Adsorption system	References
Endothermic process	Tree fern/ Basic dyes	Ho et al., 2005
	Neem leaf powder/ Methylene blue	Bhattacharyya and Sharma, 2005
	Chaff/ Methylene blue	Han et al., 2006
	Baker's yeast/ Astrazon blue	Farah et al., 2007
Exothermic process	Silica/ Basic blue	Ahmed and Ram, 1992
	Date pits/ Methylene blue	Banat et al., 2003
	Activated sludge biomass/ Basic yellow	Chu and Chen, 2002
	<i>Caulerpa scalelliformis</i> / Basic yellow	Aravindhan et al., 2007

Table 3.7 Thermodynamic parameters and their brief descriptions

Thermodynamic parameter	Calculated value	Meaning
Adsorption enthalpy, ΔH°	Positive	Endothermic phenomenon
	Negative	Exothermic phenomenon
Gibb's free energy, ΔG°	Positive	Non-spontaneous
	Negative	Spontaneous
Entropy, ΔS°	Increase	Chaotically arrangement
	Decrease	Ordered arrangement

Table 3.8 Past researches on the adsorption thermodynamics

Adsorption system (Operating temperature)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	References
Activated carbon/ Basic Red	-27.0	53.1	264	Gupta et al., 2003
Activated slag/ Basic Red	-27.9	57.6	282	Gupta et al., 2003
Neem leaf powder/ Methylene blue	-11.3	9.40	68.8	Bhattacharyya and Sharma, 2005
<i>Rhizopus arrhizus</i> / Gemazol Turquoise blue G	-3.59	27.9	-110	Aksu and Çağatay, 2006
<i>Aspergillus foetidus</i> / Reactive black 5	-1.50	12.2	80.4	Patel and Suresh, 2008

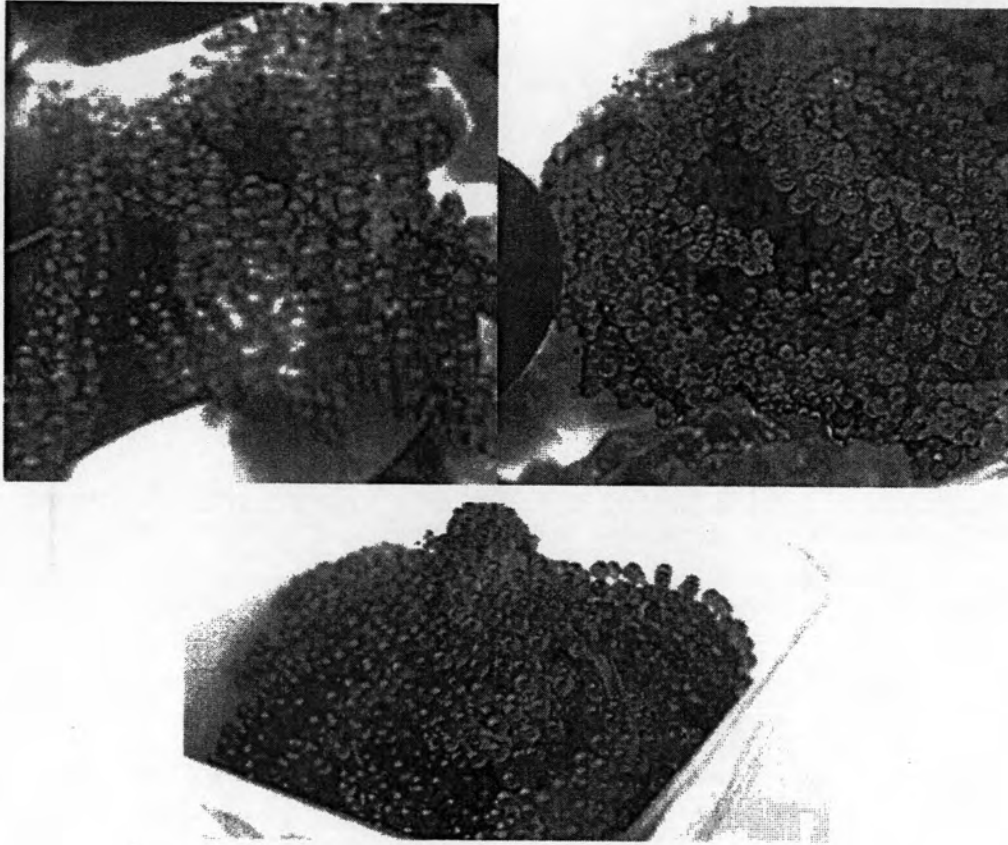


Fig. 3.1 Sea grapes or green caviar (*Caulerpa lentillifera*)