

## REVIEW OF LITERATURE

The available literature pertaining to the present study titled “**Studies on removal of brilliant green dye using marine brown macroalgal biomass *Sargassum wightii***” is presented under the following heads.

3.1. Environmental pollution

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### 3.1. Environmental Pollution

Environmental pollution is the key focus of concern worldwide. The situation is even worse in developing countries like India where little or no treatment is carried out before the discharge (Behera *et al.*, 2002). Among all the environmental pollution, pollution of water resources is a matter of great concern. The degradation of the environment due to the discharge of polluting wastewater from industrial sources is a real problem in several countries.

The main consumers of dyes are the textile, tannery, plastic, paper and rubber industries. Dyes are also used as additives in petrochemical, food, pharmaceutical, electrical, cosmetic, carpet and paint industries (Verschuere, 2009). One of the main sources with severe pollution problems worldwide is the textile industries and its dye containing waste water. 10 – 25% of textile dyes are lost during the dyeing process and 2 – 20% is discharged as aqueous effluent in different environmental components (Ahmed *et al.*, 2012). Textile industries play a very important role in degrading the water quality by releasing their effluents into rivers, lakes and oceans. Effluent color releases from textile dyeing industries which is the most evident indicator of water pollution (Ozer *et al.*, 2005). The textile industry is a high consumer of water, 90-94 % as process water, and 6–10 % as cooling water which become finally loaded with different pollutants, dyes, surfactants, acids or bases, salts, heavy metals, and suspended solids.

Dye is a colored compound that has an attraction to the substrate which is being applied. Alteration in chemical structure of dye leads to the formation of new xenobiotic compounds which creates a serious impact on environment (Bengull and Benassa, 2002). Textile dyeing effluents are highly toxic to plants, animals and soil microbes. They affect the photosynthetic functions of higher plants, reduce the soil fertility and also cause acute and chronic disorders in human beings; vomiting, haemorrhage, ulceration of skin and mucous membranes, damages the hepatic, renal and reproductive systems, mental retardation and degradation of basal ganglia of brain and liver (Murugesan and Kalichelvan, 2003; Daneshvar *et al.*, 2007).

Hence, it is necessary to develop an effective and efficient method to remove the colour from wastewater containing toxic compounds before being discharged into the environment.

### 3.2. Textile dyeing effluent toxicity and hazards to the environment

The effects and suitability of textile mill effluent from Solapur, India industrial area at different concentrations (0, 20,40,60,80 and 100%) were studied for irrigation purposes. The seed varieties of *Vigna unguiculata* (Cow pea) and *Pisum sativum* (Pea) were grown in effluent. The textile mill effluent did not show any inhibitory effect on seed germination at lower concentration. With the increase in effluent concentration, growth of seedlings was found more affected (Panaskar and Pawar, 2011).

An investigation was carried to assess the toxicity of dyeing industry effluent on seed germination and early growth of Lady's finger. Germination experiments were carried out in sterilized petri dishes containing 25, 50, 75 and 100% concentrations of untreated dyeing industry effluent. The germination percentage, growth parameters like plumule and radicle length, relative toxicity, percentage of phytotoxicity and tolerance index on the seed germination in response to dyeing effluent at various concentrations were also calculated. There was a gradual decrease in the percentage of seed germination and seedling growth with higher concentration of effluent. Relative toxicity and percentage of phytotoxicity was maximum at 100%. Growth parameter such as plumule and radicle length and tolerance index of seedlings was minimum at 100% and maximum at 25% of effluent concentration (Noel and Rajan, 2015).

The impact of different quantities of dyeing industry effluent residue (0,200, 400, 600, 800, 1000 and 1200 mg) on growth, biochemical characteristics and yield of Brinjal *Solanum melongena* were studied. The growth characteristics of *Solanum melongena* such as seed germination percentage, shoot length, root length, total fresh weight, total dry weight, leaf area index, vigour index, fruit weight and length, number of fruits were higher in brinjal grown with 800mg and lower in 1200 mg of dyeing industry effluent residue on 45th day. The chlorophyll a,b, total chlorophyll, carotenoid, total soluble protein and total sugar content of Lady's finger were also higher in brinjal grown in and lower in 1200mg (Rajan *et al.*, 2016).

Abraham *et al.* (2013) reported the effect of heavy metals (Cd, Pb, Cu) on seed germination of *Arachis hypogaeae L.* and found that Cd, Pb, and Cu significantly decreased seed germination of *Arachis hypogaeae L.* as compared to control. Increased concentration

of Cd at 75 and 100 mg/l affected the groundnut seed germination extremely. Whereas lead treatment at 75 and 100 mg/l significantly reduced the seed germination of groundnut as compared with control. Copper treatment at 100 mg/l also condensed seed germination of *Arachis hypogaeae L.* as compared with control.

The effect of textile effluent on germination and growth of *Vigna mungo L.* (Black gram) were studied. At lower concentrations, the germination ratio and growth were relatively higher than the control, but with the increase in the effluent concentration these parameters were decreased. The maximum germination and seedling growth was observed at 25% concentration along with the growth promoting effect, significantly better than control. Beyond 25% effluent, root and shoot length was decreased. The study concluded that the textile mill effluent was reported safe for irrigation purposes with proper treatment and dilution at 25% (Wins and Mnavalan, 2010).

The impact of dye effluent at various concentrations (4%, 8%, 10%, 12% and 16%) on seed germination of black gram for a period of fifteen days was done by Sasikala and Poongodi (2013). They reported that the gradual decrease in the shoot and root length of the seedlings with the increase in the dye effluent concentrations.

The effect of textile effluent was studied with respect to germination and growth parameters of cow pea *Vigna unguiculata L.* In this investigation physicochemical parameters such as colour, odour, pH, temperature, electrical conductivity (EC), total suspended solids (TSS), total dissolved solids (TDS), total solids (TS), dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), chloride, sulphate, nickel, zinc, chromium, copper, oil and grease were determined using standard procedures. At lower concentration (25%) the germination ratio and growth are significantly higher but gradual decrease in the percentage of seed germination and seedling growth with higher concentration of effluent (50,75 and control 100%) was observed. It was observed that beyond 25% effluent, root and shoot length was significantly decreased. From the study it could be concluded that the textile effluent recorded minimum growth at 100% and maximum at 25% of effluent. Thus the textile dye effluent can be safely used for irrigation purposes with proper treatment and dilution at 25% (Vigneshpriya *et al.*, 2017).

Adeogun and Chukwuka (2011) conducted an investigation on 30 days exposure of juvenile-sized *Clarias gariepinus* to textile effluent. A series of static bioassays were initially conducted with concentrations of 0.00-40.00% and the 96hr LC<sub>50</sub> value derived by probit analysis was 20.06%. Nominal concentrations of the LC<sub>50</sub> values (6.69%, 3.34% and 2.23%) and control (0.00%) were used in a static bioassay. The differential growth in saggittal otolith and somatic parameters across exposure concentrations were examined by taking somatic and otolith morphometric measurements. The weight of the right otolith of lower exposure concentrations (0.00, 2.23, 3.34%) was significantly higher ( $P < 0.05$ ) than those of the highest exposure concentration (6.69%). No other significant differences were observed across somatic and otolith parameters. The results suggested that the suitability of otolith weight as a probable early-detector of stress in natural environment.

Barot and Bahadur (2013) investigated the behavioral and histopathological effects of azodye on kidney and gills of *Labeo rohita* fingerlings. Fingerlings were exposed to sublethal concentration (2.5, 5.0 and 10 ppm) of dye for 5, 10 and 15 days. No histopathological changes were observed in control. Whereas fingerlings exposed to various dye concentration showed pathological lesions in gills and kidney tissues.

The toxicity evaluation of the wastewater samples collected from different stages of the textile industry on zebra fish was done by Zhang *et al.* (2012). Results indicated that the effluent contains pro-oxidants since the activities of the glutathione (GSH), malondialdehyde (MDA) and total anti-oxidation capacity (T-AOC) were all elevated. Besides, decrease in superoxide dismutase (SOD) and glutathione-S transferase (GST) activities observed could be interpreted as a cytotoxicity sign due to an over-production of reactive oxygen species (ROS).

Selvaraj *et al.* (2015) determine the lethal concentration of a textile industry effluent to the freshwater fish *Poecilia reticulata* by toxicity bioassay method. The LC<sub>50</sub> values of the effluent for 6, 12, 24, 48, 72 and 96 hours were found to be 73.081, 67.030, 60.398, 55.521, 49.211 and 39.726% respectively. The fishes exhibited abnormal behaviors including erratic swimming, hyper-excitation, rapid opercular movement and thick mucus covering which indicated the toxicity of the effluent. The effluent induced histopathological changes and the primary gill bar was enlarged and secondary gill bar

was detached. Liver showed cytoplasmic vacuolation and clustering of nuclei whereas in the intestine disintegration of intestinal villi and infiltration of haemocytes into the lumen.

The toxicity of textile mill effluent on economically important fish, *Labeo rohita* was reported by Bhanu and Deepak (2013). Changes were observed after 30 days of exposure, (sublethal concentration). Red blood cells, (RBC) count and Hb content were significantly decreased when compared to the control group fish. The number of white blood cells (WBC) increased in textile effluent treated fishes and thus the results are statistically significant at  $P < 0.05$  level.

Tripathy and Rao (2014) investigated the dye orange red impact on the root tip cells of onion (*Allium cepa*) through assessment of mitotic aberrations (MA). Some of the common MA observed was gradual decondensation or little condensation of chromosomal arms in abnormal metaphases and anaphases. The aberrations might be due to genotoxic assault of the dye on chromosomal condensation mechanism affecting some structural maintenance of chromosomes (SMC) proteins like condensins and/or cohesins resulting in very unusual long arms or affecting the spindle fiber formation causing disoriented mitosis (DOM). The frequencies of MA showed good correlation with the concentration of dye.

Gomes *et al.* (2013) evaluated the cytotoxic effect of the food dyes sunset yellow, bordeaux red, and tartrazine yellow on the cellular cycle of *Allium cepa*. It showed the number of micronucleated cells with bridges in anaphase and telophase and the total number of chromosomal aberrations in the *Allium cepa* root meristematic cells treated with water and with the food dyes sunset yellow, bordeaux red, and tartrazine yellow under the exposure time of 24 and 48 hours. Bulbs grown in sunset yellow, bordeaux red, and tartrazine yellow dyes had a statistically significant number of cellular aberrations as compared to their controls.

### **3.3. Textile waste water characterization**

Waste water must be tested with different physico-chemical parameters. It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose.

Currently environmental pollution is one of the issues of serious concern in the whole world since industrial activities contribute to the growth of the economy at the expense of the environment especially in developing countries. A huge amount of wastewater is discharged to the environment above the level recommended by the government. Thus the nature can eliminate as a result of increasing population and industrial developments such as the textile industry which discharges huge amount effluents with abnormal physico-chemical properties (Tekoglu and Ozdemir, 2010).

Paul *et al.* (2012) studied the physicochemical characteristics of textile industrial waste water in Solapur city. Six textile industries have been selected in the east region of Solapur city. Textile effluent from these selected industries were characterized for major pollution indicator parameters namely BOD, COD, TDS, sulphide, sulphate, chloride, hardness, alkalinity, calcium and magnesium. The results indicated that the textile industries under study area emanate effluent containing pollution indicator parameters considerably higher than standards stipulated by Central Pollution Control Board. Based on these result, it is suggested that the effluent is not suitable for discharge into environment without treatment.

The physicochemical characterization and heavy metal concentration in the effluent of textile industry was investigated by Joshi and Santani (2012). The results obtained from the physicochemical analysis of all the samples of effluent indicated high temperature, alkaline pH, and foul smell with highly colored. The TSS values in all the samples and TDS values in some samples were also very high. All the samples except one sample had high microbial load which reflects in their high BOD values. The COD values of all the samples were very high indicating high degree of pollution. The results also showed elevated levels of inorganic metals. The concentration of heavy metals also has great variability.

An attempt was made to analyze the water quality of the effluent from the textile industry, Karur, Tamil Nadu, India. In this investigation physicochemical parameters were determined using standard procedures. The result of this analysis was compared with the water quality standards of BIS (Bureau of Indian Standard). The effluent sample was dark violet in colour with objectionable odour. It showed high electrical conductivity, high

TSS, TDS, TS values, alkaline pH, high BOD and COD, low DO, high amounts of chlorides, nitrates, sulphates and also showed the presence of heavy metals, oil and grease. It was observed that all the parameters studied exceeded the BIS limits and concluded that the studied textile effluent has high pollution potential and warrants an urgent need to follow adequate effluent treatment methods before discharge into surface water for reducing potential environmental hazards (Vigneshpriya and Shanthi, 2015).

The textile wastewater was treated by using sawdust as adsorbent to analyze the various physicochemical parameters. The investigations revealed that after treatment of effluent with sawdust had lower values of all the parameters than the untreated effluent. The reduction in pollution load of treated effluent may be attributed to the adsorption of chemicals in effluent by sawdust through hydrogen bonding and ion exchange mechanism (Parihar and Malaviya, 2013).

The physical and chemical parameters of textile waste water such as pH, total dissolved solids (TDS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD), suspended solids (SS), oil and grease, calcium, magnesium, iron, manganese, sodium, potassium and total hardness were evaluated by Varma and Sharma (2011). The results revealed that the studied parameter levels are high and exceed the permissible limits does not suit for the irrigation.

The treated and untreated effluents of textile, automobile and pharmaceutical industries were analyzed for its physicochemical properties. The results revealed the treated effluents shows less inorganic compounds when compared with the untreated effluents and after treatment majority of the inorganic compounds were removed (Rohit and Ponmurugan, 2013).

Kaur *et al.* (2010) analyzed the physicochemical properties of effluents of sugar and textile industry. Analysis of the textile effluents showed that the pH (8.1 – 9.1); TSS (190 – 163); TDS (4354 – 5768), BOD (181 - 306) and COD is (3853 – 4691) whereas in the sugar effluents pH (7.1 – 9.1); TSS (301 - 494); TDS (2560 - 3978), BOD (2225 - 4526) and COD is (10896 - 16843). The values exceed the BIS values.

The textile industry effluent collected from Coimbatore, Tamil Nadu were analyzed for the physicochemical properties and the results showed the high rates of temperature (40°C), pH (7.51), electrical conductivity (9565  $\mu\text{mhos/cm}$ ), BOD (275  $\text{mg l}^{-1}$ ), COD (789  $\text{mg l}^{-1}$ ), total SS (1750  $\text{mg l}^{-1}$ ), TDS (5875  $\text{mg l}^{-1}$ ), heavy metal ions, Total hardness (  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^{-}$  and  $\text{SO}_4^{2-}$ ) and colour over the prescribed fresh water limits (Prasad and Rao, 2011).

### **3.4. Textile dye treatment**

The textile effluent was a major source of water pollution which will affect the flora and fauna existing in such environments. It is an urgent need to follow adequate effluent treatment methods before discharge into surface water for reducing potential environmental hazards.

#### **3.4.1. Physical and chemical treatment**

A wide range of physical and chemical methods have been developed for the removal of dyeing effluent to decrease their impact on the environment.

A laboratory scale experiment for the treatment of a recalcitrant and toxic synthetic wastewater containing diazo dye, acid brown 14 (AB-14) has been comparatively performed by two electro-catalytic treatment processes, namely anodic oxidation (AO) and electrocoagulation (EC) using a new batch electrochemical cell. The results indicated that the EC is more effective than AO under the optimistic condition. The results emphasize the high efficiency of AO and EC and the clean processes which are hopeful alternative for the treatment of the large volume wastewater of the textile industry (Bassyouni *et al.*, 2017).

Adsorption and improved biodegradation of dyes in wastewater was achieved with  $\text{Fe}_3\text{O}_4@\text{MIL-100}$  core-shell bio-nanocomposites, which were prepared by a step-by-step strategy and attached to the surface of bacteria via zero-length carbodiimide chemistry. The  $\text{Fe}_3\text{O}_4@\text{MIL-100}$  (Fe) nano-composite showed the excellent dye adsorption properties and the overall dye removal process followed second-order kinetics. The dye AO10 was completely eliminated from solution by the combined effects of adsorption and biodegradation within 15 and 25 h from initial dye concentrations of 25 and 50  $\text{mg/L}$ ,

respectively. The time to degrade the dye decreased from 11 h for the free microorganisms to 5 h for the bio-nanocomposite. The procedure was non-toxic, allowed for magnetic separation of the bio-nanocomposite from solution and showed good cycling performance for the removal of dye (Fan *et al.*, 2018).

Taghipour *et al.* (2018) conducted the study with a room temperature and short method (30 min) for synthesis of nanosized rod-like metal organic polymer (MOP). Reaction of 1,4-phenylenedioxy diacetic acid with zinc salt leads to the formation of  $[\text{Zn}(\text{C}_{10}\text{H}_8\text{O}_6)(\text{H}_2\text{O})_4]_n$  and subsequently was loaded on activated carbon following sonication. The combination of this new composite with sonication was applied for rapid and efficient adsorption of Bromocresol Purple (BCP) and the removal percentage was achieved of 98.69%. The experimental data were best fitted by pseudo-second order and Langmuir for kinetic model and the adsorption equilibrium isotherm, respectively.

Decolourization of real textile dyeing wastewater by modified solar photoFenton (Steel scrap/  $\text{H}_2\text{O}_2$ ) process under irradiation with sunlight was examined using batch experiments. The optimal doses of  $\text{H}_2\text{O}_2$  and steel scrap were 15 mL/L and 1 g/L, respectively at pH 3. Colour removal of 89% was obtained under optimum conditions. These results suggested that the modified solar photoFenton process proved to be efficient for decolourisation of the real textile dyeing wastewater (Ganesan and Thanasekaran, 2011).

A comparative study between the removal efficiencies of Cr (III), Cd (II) and Pb (II) from synthetic and natural wastewater by using adsorption onto the newly synthesized  $\text{Al}_2\text{O}_3/\text{PES}$  and  $\text{ZrO}_2/\text{PES}$  membranes was conducted to assess the advantages and limitations of using the metal oxides/PES membranes for heavy metals removal. The results showed that 99 % and 88 % removal efficiencies were achieved by the tested membranes for Pb (II) and Cr (III), respectively (Maximous *et al.*, 2010).

Tarap peel (TP) and oxalic-acid-modified Tarap peel (TP-OX) were used to remove brilliant green (BG) dye from aqueous solution. Surface modification of TP suggested that functional groups such as carboxyl, hydroxyl and amino were involved in the adsorption of BG onto TP. Adsorption of BG onto TP was best fitted to the Freundlich model, while experimental data for TP-OX are best described by the Tempkin model. The

maximum adsorption capacities were determined as 174 and 275 mg g<sup>-1</sup> for TP and TP-OX, respectively. Thermodynamics study indicated that the endothermic nature of adsorptions of BG dye onto both adsorbents. According to kinetics study, the adsorption mechanisms on both adsorbents followed pseudo-second-order model and thus film diffusion might have major role in the adsorption process (Dahri *et al.*, 2017).

Simultaneous removal of binary mixture of brilliant green and crystal violet using derivative spectrophotometric determination, multivariate optimization and adsorption characterization of dyes on surfactant modified nano- $\gamma$ -alumina was reported by Zolgharnein *et al.* (2015). The linear concentration range and limits of detection for the simultaneous determination of BG and CV were found to be: 1–20, 1–15 mg/L, 0.3 and 0.5 mg/L, respectively. The proposed quadratic model resulting from the Box–Behnken design approach fitted very well with the experimental data. The optimal conditions for dye removal were contact time  $t = 50$  min, sorbent dose = 0.036 g, CBG (Initial BG concentration) = 215 mg/L and CCV (Initial CV concentration) = 170 mg/L.

Synthesis of grafted natural pozzolan with 3-aminopropyltriethoxysilane for removal of Brilliant Green 1 and Reactive Black 5 from aqueous solutions was studied by Wamba *et al.* (2017). The characterization of modified pozzolan by FTIR, TGA/DTG, BET, and DRUV–vis revealed the effectiveness of grafting of amine functional group on pozzolan structure. The kinetic adsorption data were better fitted with general order for both dyes while for equilibrium models were better fitted by the Liu isotherm model. The maximum sorption capacities  $Q_{max}$  (at 50 °C) obtained with the modified pozzolan were 350.6 and 300.9 mg g<sup>-1</sup> for BG-1 and RB-5, at pH 9.0 and 2.0, respectively. The thermodynamic parameters show that the removal of dyes was spontaneous and endothermic.

Modifying cellulose with metaphosphoric acid and its efficiency in removing brilliant green dye reported by de Castro Silva *et al.* (2018). Maximal adsorption capacity at 45 °C for pure cellulose was 90.5 mg g<sup>-1</sup> at pH 10 and contact time of 40 min. Experimental isotherms better adjusted to the Langmuir model and kinetic study followed the pseudo-second-order model.

The regeneration of the spent kaolinite by different advanced oxidation processes (Fenton, electro-Fenton and electrokinetic-Fenton) was evaluated. At 100:1 H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratio and 30 min near complete dye removal (around 97%) from kaolinite was obtained by Fenton treatment. After that, a two-stage treatment for adsorption-regeneration was evaluated during five treatment cycles demonstrating its viability for regeneration of the adsorbent through dye degradation (Rosales *et al.*, 2018).

Cha *et al.* (2018) investigated the facilely prepared quince leaves derived porous carbon (QLPC) using fallen quince leaves (QLs) as cost-effective counter electrodes (CE) for the fabrication of dye-sensitized solar cells (DSSCs). By means of alkali treatment and pyrolysis process (at different temperatures of 700, 800 and 900 °C), the QLs powder undergoes chemical activation and carbonization, which results in a honeycomb-like QLPC with abundant micro/mesopores and large surface area. Simple and straightforward coating of QLPC samples onto fluorine doped tin oxide glass substrates led to improved electrocatalytic activity and good tri-iodide reduction in DSSCs. When the DSSCs were illuminated under 1 sun condition (AM 1.5; 100 mW cm<sup>-2</sup>), the device assembled with QLPC-based CE (prepared at 800 °C) showed a higher current density of 14.99 mA/cm<sup>2</sup> and power conversion efficiency of 5.52% among the other QLPC-based CEs, which are comparable with the platinum-based CE in DSSCs.

### **3.4.2. Biological treatment**

In the current scenario, there has been increased interest on bioremediation for textile dyeing effluent when compared to the physicochemical processes. Biological treatment is considered to be one the cost effective and proven technologies having potential application in waste water treatment.

#### **3.4.2.1. Adsorption by natural materials**

The feasibility of using an agricultural byproduct, almond shell (*Prunus dulcis*), as an adsorbent in removal of basic dyes, such as methylene blue (MB), methyl violet (MV), and toluidine blue O (TB), were evaluated in a batch adsorption process by Duran *et al.* (2011). The dye adsorption equilibria were rapidly attained after 30 min of contact time. The monolayer adsorption capacity of AS was found to be 51.02 mg·g<sup>-1</sup> for MB, 76.34

mg·g<sup>-1</sup> for MV, and 72.99 mg·g<sup>-1</sup> for TB by using the Langmuir model equation. The thermodynamic parameters proved that the present adsorption process was feasible, spontaneous and endothermic in nature in the temperature.

The adsorption of textile effluent using sugarcane bagasse was investigated in a batch mode of operation under the optimize condition of amount of adsorbent, initial concentration of dye, contact time, pH, and temperature on textile effluent. The experimental results showed that the high removal percentage at pH 6, temperature 35° C with a retention time of 100 minutes. The optimum dose amount of adsorbent was 0.3g/ ml. The results obtained in this work indicated that the potential use of sugarcane bagasse as a biosorbent is feasible method for the treatment of textile effluent (Vigneshpriya and Shanthi, 2016).

Wanyonyi *et al.* (2014) investigated the adsorption of congo red dye from aqueous solutions using roots of *Eichhornia crassipes*: kinetic and equilibrium studies. Batch experiments were carried out for sorption kinetics and isotherms. These experimental results showed that the adsorption process was highly dependent on contact time, adsorbent dosage, initial dye concentration and particle size. The sorption equilibrium for congo red dye by *E. crassipes* (roots) was reached within 90 minutes and adsorption efficiency up to 96% was achieved. The sorption kinetics followed a pseudo-second-order kinetic model while Freundlich isotherm model was best applicable for obtaining the equilibrium parameters. These results demonstrated that the roots of *E. crassipes* are effective, environmentally friendly and low-cost biomaterial for dye removal from aqueous dye solutions and industrial effluents.

Sartape *et al.* (2014) were carried out the study of removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. The effects of different variables, adsorbent dosage, initial dye concentration, pH, contact time and temperature etc. were investigated and optimal experimental conditions were ascertained. The Langmuir isotherm model value has given a better fit than the Freundlich model with 80.645 mg/g as maximum adsorption capacity at 299 K. The adsorption of MG on WAS was confirmed by FTIR, SEM study, as it showed the change in characterization before and after adsorption. It was found that the

Lagergren's model could be used for the prediction of the system's kinetics, while intraparticle diffusion study and Boyd plot were used to furnish the mechanistic study. Thermodynamic study concluded that the spontaneous and endothermic nature of the adsorption. This present study and comparison with other reported adsorbents concluded that, WAS may be applied as a low-cost attractive option for removal of MG from aqueous solution.

Batch experiments were carried by Kumar and Kumaran (2005) for the adsorption of mango seed kernel particles, which had reported 142.857 mg/gadsorption capacity at 303k.

Patel (2011) studied the potential of fruit and vegetable wastes as novel biosorbents. He observed the fruit and vegetable wastes produced in astronomical quantities from food processing and agriculture industries often cause nuisance in municipal landfills owing to their high biodegradability. Biosorption by these waste based adsorbents could be used as a cost effective and efficient technique for the removal of toxic heavy metals and dyes from wastewater. The results of the numerous studies on adsorbent efficiency of these bio wastes demonstrated that they apart from their wide availabilities are endowed with fast kinetics and appreciable adsorption capacities. These value added products are promising alternatives to the costly conventional methods for eco-friendly remediation of wide spectrum of pollutants.

#### **3.4.2.2. Adsorption by micro algae**

Bioremediation systems are also commonly applied to the treatment of industrial effluents including many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (McMullan *et al.*, 2001). This method has advantages like being relatively inexpensive and low operating cost.

The potential application of *Chlorella vulgaris* for bioremediation of textile waste effluent (WE) was investigated using 22 Central Composite Design (CCD) by El-Kassas and Mohamed (2014). This study addressed the adaptation of the microalgae *C. vulgaris* in textile waste effluent (WE) and the study of the best dilution of the WE for maximum biomass production and for the removal of colour and Chemical Oxygen Demand (COD)

by this microalga. The cultivation of *C. vulgaris*, presented maximum cellular concentrations  $C_{max}$  and maximum specific growth rates  $I_{max}$  in the wastewater concentration of 5.0% and 17.5%, respectively. The highest colour and COD removals occurred with 17.5% of textile waste effluent. The results of *C. vulgaris* culture in the textile waste effluent demonstrated the possibility of using this microalga for the colour and COD removal and for biomass production. There was a significant negative relationship between textile waste effluent concentration and  $C_{max}$  at  $p < 0.05$  level of significance. However, sodium bicarbonate concentration did not significantly influence the responses of  $C_{max}$  and the removal of colour and COD.

The low cost biodegradation and detoxification of textile azo dye C.I. reactive blue 172 by *Providencia rettgeri* strain HSL1 was studied by Lade *et al.* (2015). The bacterium was found to completely decolorize  $50 \text{ mg L}^{-1}$  of dye RB 172 within 20 h at  $30 \pm 0.2^\circ \text{C}$  under microaerophilic incubation conditions. Additionally, significant reduction in COD (85%) and TOC (52%) contents of dye decolorized medium was observed which suggested its mineralization. Induction in the activities of azoreductase (159%) and NADH-DCIP reductase (88%) provided an evidence for reductive cleavage of dye RB 172. The HPLC, FTIR, and GC-MS analysis of decolorized products confirmed the degradation of dye into various metabolites. The proposed metabolic pathway for biodegradation of RB 172 has been elucidated which showed the formation of 2 intermediate metabolites, namely, 4-(ethenylsulfonyl) aniline and 1-amino-1-(4-aminophenyl) propan-2-one. The acute and phytotoxicity evaluation of degraded metabolites suggests that bacterial strain favours the detoxification of dye RB 172. Thus, WB could be utilized as a low-cost growth medium for the enrichment of bacteria and their further used for biodegradation of azo dyes and its derivatives containing wastes into nontoxic form.

Garg *et al.* (2012) conducted the study to investigate the biodecolorization of textile dye effluent by *Pseudomonas putida* SKG-1 (MTCC 10510) under the conditions optimized for monoazo dye orange II color removal in simulated minimal salt medium. Maximum decolorization of initial  $100 \text{ mg dye l}^{-1}$  was achieved at optimum pH 8.0,  $30^\circ \text{C}$  and 4.0% inoculum under static conditions during 96h incubation. Supplementation with glucose at 0.4% (w/v) and ammonium sulfate (0.1%, w/v) further enhanced dye

decolorization to highest 92.8% within 96 h incubation. The strain was highly tolerant to dye up to 1000 mg l<sup>-1</sup>. Increasing dye concentration exerted inhibitory effect on bacterial growth and color removal. A direct correlation existed between bacterial growth and dye decolorization. Under above optimized conditions, 35.2% decolorization of unsterilized effluent by native microflora was achieved. The effluent decolorization marginally enhanced (41.3%) upon augmentation with *P. putida*, and substantially increased (50.2%) when supplemented with glucose and ammonium sulfate without augmentation. Maximum effluent decolorization of 69.5% occurred when supplemented with exogenous carbon and nitrogen source along with *P. putida* augmentation. Evidently, *P. putida* has great potential of textile effluent decolorization. GC-MS analysis indicated the formation of sulfanilic acid and 1, 2 naphthoquinone as orange II biodegradation metabolites and FTIR analysis revealed the presence of carbonyl and hydroxyl groups. This facultative strain could be employed for sequential anaerobic-aerobic treatment strategy leading to effective dye decolorization anaerobically and ultimate mineralization of textile dye effluent under aerobic conditions.

Adsorption characteristics of the hazardous dye brilliant green on Saklhkent mud was studied by Kismir and Aroguz (2011). The kinetic data for the adsorption of Brilliant Green on Saklikent mud supports the pseudo-first-order kinetic model and the intra-particle model at 25°C. From the kinetic data it was found that the calculated values of the maximum adsorption capacity ( $q_{e,calc}$ ) are very close to the maximum adsorption capacity ( $q_{e,exp}$ ) obtained experimentally. The experimental adsorption capacity of the Saklikent mud changed from 9.2mg g<sup>-1</sup> to 9.7mg g<sup>-1</sup> by increasing temperature from 25°C to 55°C.

Sharma and Adholeya (2011) studied the detoxification and accumulation of chromium from tannery effluent and spent chrome effluent by *Paecilomyces lilacinus* fungi. The fungus has broad pH tolerance range and could reduce Cr (VI) both in acidic (pH 5.5) and alkaline (pH 8.0) conditions. The fungus showed the ability to remove Cr (VI) (1.24 mg l<sup>-1</sup>) and total Cr (7.91 mg l<sup>-1</sup>) from tannery effluent below the detection level within 18 h and 36 h of incubation, respectively, and ability to accumulate 189.13 mg Cr g<sup>-1</sup> of dry biomass within 600 h of incubation from spent chrome effluent. At 200 mg l<sup>-1</sup> of Cr (VI) in growth media, with 100% detoxification and with only 10.54% of total Cr

accumulation in the biomass, *P. lilacinus* showed Cr (VI) reduction as a major mechanism of Cr (VI) detoxification. The time-course study revealed the log phase of the growth for the maximum specific reduction of Cr (VI) and stationary phase of the growth for its maximum specific accumulation of both the forms of Cr [Cr (III) and Cr (VI)] in its biomass. In growth media at 50 mg l<sup>-1</sup> and 200 mg l<sup>-1</sup> of Cr (VI), *P. lilacinus* showed 100% reduction within 36h and 120h of incubation, respectively. The high degree of positive correlation and statistically high degree of relationship ( $r^2 = 0.941$ ) between the fungal growth and % Cr(VI) reduction by the fungus support the role of metabolically active cellular growth in Cr(VI) reduction by the fungus. This study revealed that the strong potential of *P. lilacinus* fungi for the removal of Cr from tannery effluent and spent chrome effluent.

### 3.4.2.3. Adsorption by macro algae

Response surface methodology (RSM) was applied to optimize the operating variables on Cr(VI) uptake capacity of marine green algae *Halimeda gracilis*. A maximum percentage removal of Cr(VI) by *H. gracilis* occurs when, pH of 4.9, sorbent dosage of 2.2 g/L, agitation speed of 136 rpm and contact time at 47 min. The results showed that the sorption process of Cr(VI) ions followed pseudo second order and power function kinetics. Sorption of Cr(VI) onto *H. gracilis* biomass followed the Langmuir isotherm model ( $R^2 = 0.997$ ) with the maximum sorption capacity of 55.55 mg/g. The calculated thermodynamic parameters such as  $\Delta G^\circ$ ,  $\Delta H$  and  $\Delta S$  showed that the sorption of Cr(VI) ions onto *H. gracilis* biomass was feasible, spontaneous and endothermic. Desorption study shows that the sorbent could be regenerated using 0.2 M HCl solution, with up to 80% recovery (Jayakumar *et al.*, 2014).

*Sargassum binderi*, a species of brown seaweed was used as a low cost biosorbent to remove a basic dye, Basic Yellow 11 (BY11). Various parameters such as pH, initial concentration and sorbent dosage were conducted using batch sorption process. In this study, *S. binderi* exhibited good performance (almost 100% of BY11 removal) with 1 g of sorbent dosage in 100 mg L<sup>-1</sup> of dye solution, pH of the solution, however, does not seem to have high influence on removal of BY11. From the analysis, the sorption of BY11 onto the *S. binderi* was found obeyed Freundlich model with coefficient correlation value of

0.9959 which indicates heterogeneous layers of sorption. The sorption process followed pseudo-second-order kinetic which involved chemisorption. The study concluded that *S. binderi* was proved to have high sorption efficiency towards BY11 and thus, it can be categorized as one of the promising biosorbent to be applied in treating the effluent discharge from industries (Tan *et al.*, 2009).

The potential of a brown alga, *Sargassum oligocystum* harvested from Persian Gulf used for the adsorption of copper ions from aqueous solutions. The adsorption kinetic and isotherm and the characteristics of the biomass prepared from *S. oligocystum* (BSO) have been investigated. Brunauer, Emmett, and Teller (BET) showed that BSO was a mesoporous adsorbent with surface area, a total pore volume, and an average pore diameter were 0.487m<sup>2</sup>/g, 1.423cm<sup>3</sup>/g and 12.5nm, respectively. Fourier transform infrared spectroscopy (FTIR) analysis showed that there were many active functional groups such as alcohol and phenol groups, carbonyl, ethers, and esters on the BSO. Batch tests demonstrated that the Langmuir isotherm model best represented the equilibrium data with maximum copper ions adsorption capacity of 8.23 mg/g. the results concluded that BSO is an easy prepared adsorbent and could be an option for the treatment of Cu<sup>2+</sup> laden wastewaters (Ramavadi *et al.*, 2015).

The removal of textile dye methylene blue from aqueous solution using adsorbents such as alumina, *Ulva lactuca* and *Sargassum* sp was studied by Tahir *et al.* (2008). The batch technique was adopted under the optimize condition of amount of adsorbent, stay time, concentration, temperature and pH. By using UV spectrophotometer, concentration of dye was measured before and after adsorption. The removal data were fitted into the Langmuir and Freundlich adsorption isotherm equations. The values of their corresponding constants were determined. Thermodynamic parameters like free energy (G), enthalpy (H) and entropy (S) of the systems were calculated by using Langmuir constant (K). The values of % removal and KD for dye systems were calculated at different temperatures ranging (303 - 318 K) with the intervals of 5 ± 2°C. The present study shows that about 96% removal of dye was obtained by using biosorbents.

The removal of AB1 with brown macroalgae *Sargassum glaucescens* and *Stoechospermum marginatum* was studied using a batch system. The effects of parameters

such as initial pH (in the range 2–10), contact time (within 90 min), biomass dosage (in the range 1–9 g L<sup>-1</sup>), initial dye concentration (in the range 10–50 mg L<sup>-1</sup>), particle size of biosorbent (0.53–500  $\mu$ m) and agitation speed (from 70 to 180 rpm) on the adsorption capacity of AB1 were investigated. The equilibrium data indicated that the Freundlich model provided the best correlation of the experimental data for both biosorbents. The biosorption kinetic data were successfully described with pseudo-second order model (PSORE) for two biosorbents. Thermodynamic parameters showed adsorption of dye was feasible and endothermic at all temperatures (283–313 K) for both biosorbents. A decrease in particle size of biosorbents increased acidic dye removal capacity. The agitation speed influences AB1 sorption capacity and optimum agitation speed observed at 130 rpm among different agitation speed (70–180 rpm). FT-IR analysis demonstrated the involvement of different functional groups, mainly hydroxyl, carboxyl and amine groups. These results confirm that these algae have a good potential for removal of AB1 from aqueous solution at low dye concentration (Daneshvar *et al.*, 2012).

Adsorption of methylene blue using *Sargassum muticum*, an invasive macroalga in Europe, was reported by Rubin *et al.* (2005). Different pre-treatments, protonation and chemical cross-linking with CaCl<sub>2</sub> or H<sub>2</sub>CO<sub>3</sub>, have been tested in order to improve the stability as well as the adsorption capacity of the algal biomass. The equilibrium binding has been described in terms of Langmuir and Freundlich isotherms depending on the algal pre-treatment. Moreover, it has been found that adsorption kinetics could be described according to the first order Lagergren model, from which the rate constant and the adsorption capacity were determined. Finally, simple empirical equations were obtained to evaluate the amount of methylene blue removed at any initial concentration and reaction time. The results obtained have shown that this type of material has a high adsorption capacity for methylene blue dye, this feature together with the short times needed to reach the equilibrium suggest that *Sargassum muticum* can be used as a low-cost biosorbent in wastewater treatments.

The comparative studies on the removal of textile effluents by various eco-friendly adsorbent such as sawdust, neem cake, rice husk and *Sargassum wightii*, the low cost, available and renewable biological adsorbent were reported by Nagarani *et al.* (2012). Batch experiments were carried out for sorption kinetics and isotherms. Operating

variables were time and pH. Biosorption capacity seems to be enhanced by decreasing the pH. Maximum color removal was observed at pH 3–5. Experimental sorption kinetic data were fitted to pseudo second order for all adsorbents ( $R^2=0.987$ ).

The malachite green dye adsorption from an aqueous solution onto activated *Enteromorpha* carbon using batch adsorption method was studied by Jayaraj *et al.* (2011). Adsorption kinetics and equilibrium were investigated as a function of initial dye concentration, pH, contact time and adsorbent dosage. Kinetics studies indicated that the adsorption followed pseudo second order reaction. Equilibrium data was analyzed using Langmuir and Freundlich isotherm models. The adsorption capacity of *Enteromorpha* was found to be 94.74%. On the basis of experimental results and the model parameters, it can be inferred that the carbonaceous *Enteromorpha* is effective for the removal of malachite green from aqueous solution.

Kumaraguru and Sureshkumar (2014) investigated the kinetics, modeling, thermodynamic analysis and optimization of biosorption parameters for biomass of *Sargassum wighiti* using response surface methodology. In this study, the central composite design matrix (CCD) and response surface methodology (RSM) by design expert version 8.0.5 (Stat Ease, USA) have been applied to design the experiments to evaluate the interactive effects of five important variables viz., sorbent size (0.176 - 1.503 mm), sorbent dosage (30 - 70g/l), temperature (25 - 45°C), contact time (2 - 10 hrs) and agitation speed (50 - 250 rpm) for full response surface estimation on biosorption of chromium (VI) ion using the dry biomass of *sargassum wighiti*. Batch mode experiments were carried out to assess the biosorption equilibrium. Kinetic and isotherm studies were carried out, the thermodynamic parameters like standard Gibb's free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were evaluated. The optimum conditions for maximum uptake of chromium (VI) ions from an aqueous solution of 100 mg/L were as follows: sorbent size (0.5284 mm), sorbent dosage (4.8798 g), temperature (34.16°C), contact time (5 hours 58 minutes) and agitation speed (151.2 rpm). Analysis of variance (ANOVA) showed a high coefficient of determination value ( $R^2 = 0.9446$ ) and satisfactory prediction second-order regression model was derived.

Kousha *et al.* (2012) conducted an experiment using the response surface methodology (RSM) based on three-variable-three-level Box–Behnken design employed to interpret the adsorption characteristics of Acid Black 1 (AB1) dye onto three brown macroalgae viz., *Nizamuddin zanardini*, *Sargassum glaucescens* and *Stoechospermum marginatum*. The effects of three independent variables, viz. biomass dosage, dye concentration, and initial solution pH were studied for the removal of AB1 dye by the three macroalgae. A second-order polynomial model successfully described the effects of independent variables on the AB1 dye removal. The maximum experimental dye removal efficiency of 99.27, 98.12 and 97.62% for *N. zanardini*, *S. glaucescens* and *S. marginatum*, respectively, was obtained, which was in agreement with the calculated values. The results of the study suggested that these macroalgae can be used as an efficient biosorbents for dye removal from aqueous solution.

Gajare and Menghani (2012) were carried out an experiment to determine the biosorption of malachite green by naturally grown algal biomass from Girna River, Jalgaon District, Maharashtra. The samples were assessed for the diversity of algal forms. The biomass was sun dried in laboratory and subjected to various chemical pretreatments. They reported that chemical treatment to biomass was found to alter the biosorptive properties of biomass. Acid treatment was emerge as an effective treatment enhancing dye removal capacity of biomass (>90 mg of dye / g biomass). Kinetic studies indicated that the process was requiring <45min for >85% of sorption while process reached an equilibrium in <50 min of contact. This study also revealed that the biomass could be reused at least four times without altering the sorption properties. Certainly, these results have developed a trust with algal biomass, otherwise is a problem of algal blooms in rivers and ponds, in the treatment of dye waste waters.

Aswin (2015) conducted an experiment on biosorption capacity of *Sargassum longifolium* for textile effluent. The measure of dye adsorbed at equilibrium was found to change from 67.32 mg/g to 581.61mg/g with expanding introductory dye amassing of 20-100 mg/L for a biomass of 0.1 g. It was found that the biomass demonstrated greatest adsorption limit at 100 mg/L colour answer for a sorbent dose of 0.1g at 20°C with an agitation speed of 100 rpm. The equilibrium was found to fit well with Freundlich when compared with Langmuir adsorption isotherm. The chemical kinetics of the adsorption

procedure was likewise concentrated on and the response was found to take after the pseudo second order kinetics.

The biosorption efficiency and capacity of Methylene blue (MB) dye from aqueous solution by untreated and pretreated (physical and chemical) brown (*Nizamuddinina zanardinii*), red (*Gracilaria parvispora*) and green (*Ulva fasciata*) algae was investigated. Among the seventeen chemicals tested for pretreatment, sodium thiosulfate, isooctane and 1-butanol were found to be the most effective chemicals for brown, red and green macroalgae, respectively. Different concentrations of these chemicals and sodium chloride were further examined in the range of 0–2 M to obtain the best concentration for pretreatment. Results from this study demonstrated the potential utility of macroalgae for MB dye removal from water (Daneshvar *et al.*, 2017).

### **3.5. Factors affecting adsorption**

#### **pH**

pH is an important parameter which affects the adsorption process especially for cationic dye adsorption. Cationic dye possessed positive charge groups which play an important role in binding with surface charge of sorbent. These surface charges were greatly influenced by pH of the solution (Wang *et al.*, 2008). Decrease in the removal of dye with increasing pH is possibly because the surface is negatively charged, thus enhancing the Columbic repulsions with the dye anions.

#### **Temperature**

Temperature is also one of the controlling parameters in adsorption process. According to Durairaj and Durairaj (2012) increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles owing to the decrease in the viscosity of the solution. An increased number of molecules may acquire sufficient energy to undergo an interaction with active sites at the surface. The decrease in biosorption of dyes at high temperatures may be due to the weakening of adsorptive forces responsible for the adsorption of dye molecules on the surface of biosorbents. This can also be due to the fact that deactivation of biosorbent active sites takes place, which leads to the decreased biosorption at higher temperatures (Asgher and Bhatti, 2012).

### **Adsorbent dose**

The increase in efficiency at higher adsorbent concentrations was attributed to the availability of more adsorption sites at those concentrations, while the decrease in adsorption density with a rise in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the adsorption process. Biosorbent dose plays a very important role in the process of biosorption. The dye biosorption capacity decreased at higher biosorbent doses due to the aggregation of the biomass which results in the decrease in active sites on the surface of biosorbent available for the attachment of dye molecules. Another important factor is that at high biosorbent dose, the available dye molecules are insufficient to completely cover the available binding sites on the biosorbent, which usually results in low solute uptake (Tangaromsuk *et al.*, 2002).

### **Initial dye concentration**

The initial dye concentration provides an important driving force to overcome all the mass transfer resistances of the dye between the aqueous and solid phases. Hence, a higher initial concentration of dye may enhance the adsorption process. At the lower concentration, the ratio of the initial moles of dye compared to the available surface area is low; therefore, the subsequent fractional sorption becomes independent of the initial concentration. However, at the higher concentration the available sites for sorption will be less for the dye present in it, hence, the percentage dye removal is dependent on the initial dye concentration (Gautam *et al.*, 2013).

### **Contact time**

The contact time between dyes and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of dyes and establishment of equilibrium in short period signifies the efficiency of the adsorbent for its use in wastewater treatment. Kavitha and Namasivayam (2007) explained that the initial rapid phase may be due to the increased number of vacant sites available at the initial stage. Consequently there exists an increased concentration gradient between the adsorbate in solution and the adsorbate in the adsorbent.

### **3.6. Brilliant green- the candidate dye**

Brilliant green is a cationic dye used for various purposes which includes biological stain, dermatological agent, veterinary medicine, and an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus. It is also extensively used in textile dyeing and paper printing industry. Brilliant green dye causes several effects on human beings including irritation to the gastrointestinal tract, nausea and vomiting, irritation to the respiratory tract and irritation to skin (Narat, 1931 and Mittal *et al.*, 2008). Brilliant Green may form hazardous products like nitrogen oxides, and sulfur dioxides due to decomposition on heating (Mane *et al.*, 2007). Therefore, the removal of brilliant green dye from aqueous solution becomes environmentally important and the removal of dye using seaweed as adsorbent material is the focus of the present study.

### **3.7. Seaweed *Sargassum wightii*- an adsorbent**

Seaweed *Sargassum wightii* is the marine macroalga known for its photosynthetically efficient nature which play the major role in dye adsorption process. This was utilized as an effective biosorbent for the removal of brilliant green dye from the aqueous solution. The cell wall of seaweeds have some organic functional groups, which are accompanying along with starch, alginic acid and proteins which can be help them to remove the organic pollutants from waste water (Tan *et al.*, 2009).