

REVIEW OF LITERATURE

Increased population and modernized civilization have a tendency to give rise to the blooming of textile sectors in India. An estimate shows that textiles account for 14% of India's industrial production and about 27% of its export earnings. India is the second largest producer of cotton yarn and silk and the third largest producer of cotton and cellulose fiber. The textile industry is one of the foremost sectors in the Indian economy. The silk industry comes under the section of textile industry. The risk factor in the silk industry is linked with the process of dyeing such as soaking, degumming, dyeing and finishing where the chemicals are used. These chemicals can cause damage, if they are not appropriately treated before discharged into the environment. The untreated effluent can seriously affect the environment. When it is discharged into the land, it contaminates the soil and affects the growth of plants (Thanushree *et al.*, 2013).

Wastewater discharged from the silk industry is the source of aesthetic pollution associated to color. The salt and the heavy metal in the wastewater are toxic to aquatic life. Some of the dyes are carcinogenic and thus cause severe health problems (Alinsafi *et al.*, 2005). The current technologies available for the treatment of dyeing effluents before discharging are of great consequence in decreasing pollution load and production costs. Conventional technologies with various combinations of physical, chemical and biological methods are to treat the wastewater but these methods need high capital and operating costs. Thus the efficient technique to remove dyes from the large volumes of wastewater at low cost is preferable alternatives (Bizuneh, 2012).

The review of literature pertaining to the present study “**Biofertilizer mediated remediation of silk dyeing industrial effluent and its effect on selected green leafy vegetables**” is discussed under the following headings:

2.1. Industrialization and its impact on environment

2.2. Silk dyeing industry

2.2.1 Process of dyeing

2.2.2 Chemical dyes and Heavy metals in effluent

2.2.3 Prevailing effluent treatment strategies

2.2.4 Effect of silk dyeing effluent on plant growth

2.2.5 Effect of silk dyeing effluent on fish

2.3. Biodegradation of Silk dyeing effluent and its importance

2.4. Effect of Biofertilizers as biodegraders

2.5. Importance of green leafy vegetables

2.1 Industrialization and its impact on environment

Industrialization is essential to a nation's economy because it serves as a vehicle for the development. Soil nutrient quality has been affected by industrialization. There are so many major and minor industries in our country that contaminates the environment and deteriorate our life (Rajbala and Bhaskar, 2012). The textile industry in India is one of the oldest industries. The silk dyeing industry is one among the textile industries. It provides direct employment to almost thirty million people. India's dyeing industry produces all type of dyes and pigments. Production of dyestuff and pigments in India is near to 80,000 tones. India is the second largest exporter of dye stuffs after China. The textile industry accounts for the largest consumption of dye stuffs (nearly 80%). During the last decade, environmental issues associated with dye stuff production and application have developed significantly and is the major driving force affecting the textile dye industry (Thiripurasundari *et al.*, 2013). The dyestuff usage has been rising day by day because of tremendous increase of industrialization and man's urge for color. Public concern about environmental issues has enforced several small-scale industries to wind up (Bizuneh, 2012).

Wastewater from the textile industries constitutes a threat to the environment in large parts of the world (Nilsson *et al.*, 2006). The environmental pollution was caused by the release of various chemicals as a result of silk industrial process which has now become a persistent environmental contaminant. Due to rapid industrialization and urbanization, a lot of chemicals including dyes and pigments are released. The total quantity of wastewater production from dyeing activity is reported to be about 600 m³/day and from the bleaching activity is 100 m³/day (Mohana *et al.*, 2008). Small scale industries adopt ineffective technologies and therefore pollute more than large scale units (Shivaraju *et al.*, 2011).

The dye effluent contaminates the surface and the ground water and makes it unfit for irrigation and drinking (Mathur and Bhatnagar, 2007). The silk dyeing industrial effluent has to be discharged after proper treatment. The dyes are stable to light, heat and oxidizing agents and it is complicated to remove the dyes from the effluents. This requires effective and economic treatment of the effluents containing various dyes (Shanooba *et al.*, 2011).

2.2 Silk dyeing industry

The dyeing industry has been referred as one of the four major polluting industries in India (Subhathra *et al.*, 2013). A total of 120 dyeing units function in Salem district with 70 in corporation limits. Manual dyeing is carried out in most of the units and several are also functioning in residential areas. But none of the units follow the 'zero discharge' pattern, as the industrial effluent is let off into drains directly which, in turn, pass through the residential areas. After the closure of many dyeing units in Tirupur and Erode districts over the discharge issue, many started to move to Salem and started functioning in agricultural lands. More than 10 such illegal dyeing units were found and demolished by the Tamil Nadu Pollution Control Board officials. Wastewater treatment plant installation and commissioning cost is in the range of 40-100 lakhs, 100-200 lakhs and 200-300 lakhs for small (below 300m³/day), medium (300-600m³/day) and large (above 600m³/day) scale textile dyeing industries. Total expenses incurred for the water treatment and recovery is about INR 80/m³ effluent (Ranganathan *et al.*, 2007). The total quantity of fabric processed in the unit is 1500–2000 kg/day and the volume of effluent generated is of the order of 100-200m³/day. Effluents are segregated into dye bath wastewater and wash water and treatment is effected consequently. The total quantity of color consumption is expected to be about 250 kg/day (Jai Prakash *et al.*, 2012).

In order to maximize the health and the environmental benefits associated with the use and discharge of wastewater, several legislations and guidelines have been developed, both at international and national levels. Many treatment plants were designed to remove the effluent by physical method and the addition of chemicals in chemical method. Since the former method is costly and the latter treatment is known to increase sludge volume and often results in sludge with poor settling and dewatering characteristics and depression of the pH, biological treatment is adapted in recent years. Since large amount of waste products are passed through sewage treatment systems on a daily basis, appropriate nutrient

removal strategy is vital for the preservation of the lakes, streams, rivers and other water receiving bodies.

2.2.1 Process of dyeing

The silk yarn processing involves soaping of yarn, bleaching and dyeing. The raw silk is composed of Fibroin (70-80%), Sericin (20-30%), Waxy matter (0.4-0.8%), Carbohydrates (1.2-1.65%), Inorganic matter (0.7%) and Pigments (0.2%). Figure 1 and plate 1 show the various processes of silk dyeing.

Degumming

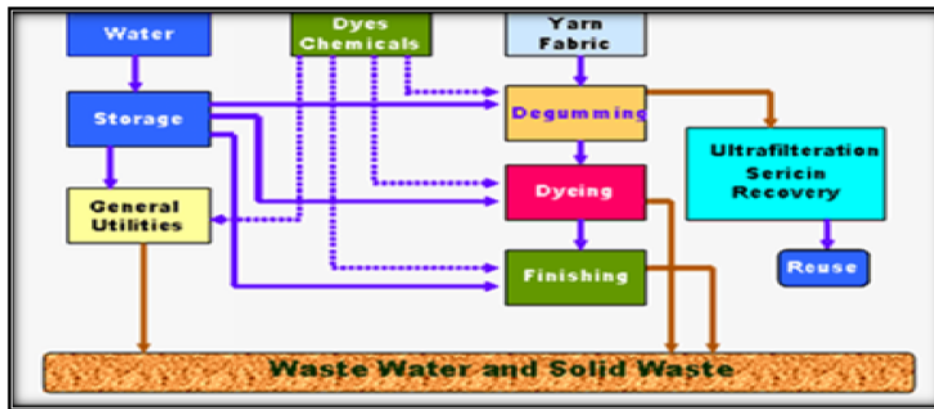
Prior to the dyeing of raw silk, a process of Boiling off (Degumming) is adopted, which removes the sericin and forms 25% of the total weight of the raw silk. Sericin is insoluble in water. It is comparatively easily hydrolyzed whereas the long protein molecule of sericin is broken down into smaller fractions, which are easily dispersed or solubilized in hot water. Hydrolysis of proteins can be carried out by treatment via acids, alkalis and enzymes. Acids tend to attack vigorously which are non-specific. Alkalies also attack sericin and fibroin. Removing the gum improves the sheen, color and texture of the silk which can provide a protective layer. It is typically left on the silk until it is ready to dye. In some cases, the fabric is woven to completion and then degummed to shield the yarn from abrasion on the loom. This process is involved in removing these impurities. However, the difference in the rate of hydrolysis is large enough to control the reaction. The conventional process is still widely followed by modern variation is to soak silk to the near boiling soap solution for about two hours or more. There are two methods of degumming raw silk.

- i) Chemical degumming
 - a) The bag or the tank method and the stick or the foam method. The silk skeins are packed in linen mesh bags (about 600 grams of silk per bag) and then dipped in the soap solution with the material ratio 30:1.
 - b) In the second method, the skeins are hung on the sticks across an open container full of soap solutions positioned on fire.

The degumming with soaps in the presence of mild alkalies like soda ash is practiced. Degumming with alkalies is a function of pH, temperature and duration of treatment. The pH should be kept at the level of 9.5 to 10.5.

Figure 1

Flow diagram of silk dyeing processes



If the level is below 9.5, then the method of removing sericin will be slow. If the pH is more than 10.5, the weight loss will be greatly increased. The degumming lost in this process is generally 20-25%. In certain cases, entire silk gum is not removed, but only sufficient amount is removed to make the silk soft, lustrous and workable in dyeing and bleaching. This is called as “Soupling” in which only 10% to 15 % of the gum is removed. In addition to removing of the soil and additives are used at the same time of weaving silk. The scouring removes any sericin (gum) that remains on the silk. Often a quantity of the natural gum has been allowed to remain on the silk fibre to give it additional body and to make it easier to handle in spinning and weaving.

ii) Enzymatic degumming is promising as an eco-friendly fibre-gentle process where proteolytic enzymes that are efficient under alkaline, neutral and acidic conditions are being used. With the local availability of the enzymes at a reasonable price, this process has a commercial potential in India. Being large molecules, enzymes do not penetrate into the interstices of the fabric and hence are suitable for yarn degumming only. A critical control of the pH and temperature is required to recognize the full potential of the enzymes requiring use of sophisticated machinery such as the Mezzera yarn-dyeing machine. Since most of the enzymes are efficient at a comparatively low temperature of about 60°C, they are less energy-intensive (Gulrajani, 2008).

Bleaching

In this step, removal of unwanted colour from the fibres by using chemicals such as sodium hypochlorite and hydrogen peroxide. The popular method is used to prepare

bleaching liquor by the use of hydrogen peroxide with or without soap i.e ammonia or sodium sulphate. The silk is bleached in the mentioned solution at 40°C temperature gradually raised to 90°C. The silk is then kept in the cooling liquor overnight, washed and soaped. Another bleaching process is sulphate staving, in which initially the skeins are hung on rods in closed chamber and exposed for a day in sulphurous acids produced by the burning of sulphur (Datta and Mahesh, 2007).

Dyeing

This is the final step of adding different color to the fibres, which normally requires large volumes of water not only in the dyebath, but also during the rinsing step. Dye bath solution needs dyes, alkali and sodium salt. Quantity of salt (sodium chloride) used depends on the requirement of color shade. Depending on the dyeing process, many chemicals like metals, salts, surfactants, organic processing assistants, sulphide and formaldehyde may be supplemented to improve dye adsorption onto the fibres (Dos Santos *et al.*, 2007). The absorption of the dye from the dyebath, as well as helping the dye set on the fabric is achieved in this step. The dye bath will become much clearer and this method is called exhausting. The dye leaves the water and enters into the silk. These are the dyed skeins after they have been rinsed, wrung out tightly and partially dried.

Finishing

The finishing of the dyed skein are broadly classified as

- a) **Mechanical finishing:** The mechanical finishing is to improve certain desirable qualities like drape, fall, handle, feel, stiffness, weight.
- b) **Chemical finishing:** The chemical finishing is to impart the desirable effect, such as antcrease and flame retardant qualities. However, some finishes have been introduced to give new look to the products such as the stone-wash, crumpled look or the peach finish.

After all the processes, two types of effluent are let out from the silk dyeing process. Major portion in the process release effluent of alkaline nature and minor portion will be acidic nature. Currently, the entire quantity of untreated waste water is being discharged into the underground water (Shivaraju *et al.*, 2011).

Plate 1

Different processes involved in silk dyeing



Dye bath preparation



Bleaching and Drying



Dyeing



Manual squeezing of excess water



Drying of dyed skein



Dyed silk yarn making into spool

2.2.2 Chemical dyes and Heavy metals in effluent

Some dyes have low-level of metal impurities that are present in terms of functionality and color rather than necessity. About 2% of commercial direct dyes have metal as an integral part of the dye chromophore. Various processing of textiles consume large volume of water, dyes and chemicals (Palanivelan *et al.*, 2013). Perhaps the mainly studied chemical pollutants with biomarkers are heavy metal stress which leads to pointed changes in the activities of certain antioxidative enzymes notably activity upon toxic exposure. Accumulation of heavy metals over prolonged time becomes hazardous to animals and human health after entering in their body systems throughout food chain. Heavy metal pollution of agricultural soils is one of the most severe ecological problems faced worldwide. Bioaccumulation of metals in fauna and flora happens if the rate of uptake of heavy metals by the organisms exceeds the excretion phase (Fatima and Ahmad, 2005).

2.2.3 Prevailing effluent treatment strategies

The control of water pollution has become an increasing consequence in recent years. The release of dyes into the environment constitutes only a small proportion of water, but dyes are visible in small quantities due to their intensity. Currently, removal of dyes from effluents is by physico-chemical methods which consist of ozonation, photooxidation, electrocoagulation, adsorption, froth flotation, reverse osmosis, ion exchange, membrane filtration, flocculation, etc., employed for dye decolorization are less efficient, costly and generate secondary solid waste (Mittal *et al.*, 2005). The elimination of textile dyeing effluent and heavy metals mainly concentrated on the development of an efficient and cost effective removal process (Maier *et al.*, 2004). Physical and chemical methods of dye removal are effective only if the effluent volume is small, therefore are unable to be used by large-scale industry. This limits the use of such methods which are often very costly. Although the dyes are removed, the accumulation of concentrated sludge creates a disposal problem. So there is a need for alternative treatments that are effective in removing dyes from large volumes of effluents and are low in cost, such as biological systems and also tightening government legislation is forcing textile industries to treat their waste effluent effectively. Biological systems efficiently degrade textile wastewaters are preferable because they are cheaper and produce lower amounts of sludge, as sludge treatment and

disposal is a key element in the global cost of treatment. However, the advanced biological processes have established increasing attention due to low cost, effectivity, less sludge generation and ecofriendly nature (Lotito *et al.*, 2012).

2.2.4 Effect of silk dyeing effluent on plant growth

Crops and vegetables grown in the agricultural fields irrigated by textile effluent are adversely affected qualitatively and quantitatively. Impact of the textile wastewater on agricultural crops has been studied previously by several researchers. The dyeing effluent containing the heavy metals are toxic to the plants which inhibit germination, reduce growth, generate oxidative stress, decrease protein content, inhibit photosynthesis and alter enzyme activities (Panda and Choudhury, 2005). Reactive oxygen species (ROS) are produced in plants in response to the damaging effects of environmental stresses and plants have developed a variety of antioxidant defense mechanisms in response to stress. The antioxidants present in the crops are good indicators as biomarkers of the oxidative stress exerted in plants induced by effluent treatment (Sangeetha *et al.*, 2012).

Vegetables, especially those of leafy vegetables grown in heavy metals contaminated soils, accumulate higher amounts of heavy metals such as Cadmium (Cd), Lead (Pb), Zinc (Zn) and Nickel (Ni) than those grown in uncontaminated soils because of the fact that they absorb these metals through their roots (Pandey, 2006). When these plants are consumed, it causes a serious health risk to human health (Demirezen and Ahmed, 2006). Cowpea, okra raddish, spinach, chickpea, pea and wheat grown in heavy metals contaminated soils influence the biomass, yield and metal distribution in different parts of the crop plants (Singh and Agarwal, 2006).

2.2.5 Effect of silk dyeing effluent on fish

Most of the water used in the process of dyeing is discharged as highly colored effluent from the textile industry. The colored effluents are not only aesthetically unacceptable, but also prevent the passage of sunlight through contaminated waterways. This reduces the photosynthetic activity of aquatic flora, which causes depletion of dissolved oxygen, ultimately leading to death and putrefaction of aquatic animals (Garg and Tripathi, 2011). Unless textile effluent is treated properly, toxic metals present in the dyes reach to aquatic environments and pose serious threats to aquatic lives. The aquatic habitats are killed by the toxic chemicals with the resultant disruption of the aquatic ecosystem and

its food chain. The decomposition of the organic materials by microorganisms in the aquatic ecosystem leads to the lowering of the level of dissolved oxygen, which in turn inhibits the growth or cause death to the aquatic habitats (Onuegbu *et al.*, 2008).

2.3. Biodegradation of Silk dyeing effluent and its importance

Currently, much research has been focused on the biodegradation of the industrial effluents. The dyeing effluent includes strong dyes which are natural and xenobiotic compounds. However, the release of coloured wastewater represents a severe environmental problem and a public health concern. Colour removal, especially from textile wastewater, has been a big challenge over the last decades, and up to now there is no single and economically attractive treatment that can effectively decolorize dyes (Dos Santos *et al.*, 2007). Microbial components of mixed microbial cultures acclimated with dyeing wastewater were found capable of decolorizing dyes via biotransformation and biodegradation (Asgher *et al.*, 2007).

Bacterial degradation of dyes is often initiated under static / anaerobic conditions by an enzymatic transformation reaction (Carvalho *et al.*, 2008). Biodegradation is a biologically mediated breakdown of chemical compounds. When this process gets completed it is called mineralization i.e. the total breakdown of organic molecules into water, carbon dioxide and any other inorganic end products. These methods have the potential to mineralize dyes to harmless inorganic compounds like carbon dioxide, water and the formation of a small quantity of relatively insignificant amount of sludge. The attractive features of biological treatment or biodegradation are low cost, renewable and regenerative activity without any secondary hazard (Andleeb *et al.*, 2010).

2.4. Effect of Biofertilizers as biodegraders

Plant growth promoting rhizobacteria (PGPR) are a group of bacteria that enhance plant growth and yield via various plant growth promoting substances as well as acting as biofertilizers. The use of beneficial soil microorganisms such as PGPR for sustainable and safe agriculture has increased globally during the last couple of decades. PGPR as biofertilizers are well recognized as efficient soil microbes for sustainable agriculture and hold great promise in the improvement of agriculture yields (Jay, 2013). Many fluorescent *Pseudomonas* strains have been reported as plant growth enhancing beneficial rhizobacteria. They are studied widely in agriculture for their role in crop improvement as they stimulate

plant growth either by producing plant growth promoting hormones, fixing atmospheric N₂ or suppressing plant pathogens. The ubiquitous rhizosphere microflora forming symbiosis with plant roots, act as biofertilizers, bioprotectants and biodegraders. PGPR nitrogen fixing bacterial symbionts help in sustainable plant growth on nutrient-poor heavy metal contaminated industrial sites and it was found that the plants surviving on such sites were associated with N-fixing rhizobacteria (Khan Abdul, 2011).

Bacterial biodegradation of textile dyes is an attractive and inexpensive method. Bioaugmentation involves the introduction of microorganisms to contaminated media to promote the degradation of contaminants (Anna *et al.*, 2012). Much better results are obtained during bioaugmentation processes with the use of soil microorganisms capable of pollution degradation. Development of crop and eco-specific bioinoculants (biological control agents, biofertilizers, biodegraders) is perceived as one of the most exciting areas owing to its potential of solving multifarious agricultural and environmental problems concurrently (Dinesh and Maheshwari, 2011).

2.5. Importance of green leafy vegetables

Leafy vegetables are a valuable part of the diet owing to their nutritive values which play an important role in the human diet. They are highly diverse in species, varieties and agro-ecological requirements. The quality of leafy vegetables depends on internal and external quality. It is well known that red and dark green colored leafy vegetables are richer in nutrient content than lighter colored vegetables (Kaur and Kapoor, 2011). Due to their dietary importance, many scientific studies have been carried out on the nutritive values of green leaves (Gayathri *et al.*, 2008).

Green leafy vegetables (GLVs) are rich in micronutrients and are nature's gift to mankind that provides more vitamins than any other food. They are a rich source of calcium, iron, β -carotene, vitamin C, dietary fiber and many trace elements. GLVs are rich in bioactive, non-nutritive, health enhancing factors such as antioxidants, phytochemicals, essential fatty acids and dietary fiber (Gupta and Prakash, 2009).

GLVs have long been known as the cheapest and the most abundant potential sources of vitamins and minerals. The ethno botanical reports offer information on medicinal properties of GLVs like antidiabetic, antihistaminic, anticarcinogenic,

hypolipidemic and antibacterial activity. GLVs are also rich sources of carotenoids (Ramesh and Satakopan, 2010).

Brassica juncea

It is known as mustard greens, Indian mustard, Chinese mustard and leaf mustard. The leaves, the seeds and the stem of this mustard variety are edible. Cultivars of *Brassica juncea* are grown as greens and for the production of oilseed (Heimler, 2007). It is being grown for its seeds which yield an essential oil and condiment. Mustard oil is one of the major edible oil in India (Jeffery *et al.*, 2008). Brassica are highly regarded for their nutritional value. They provide high amounts of vitamin C and soluble fiber and contain multiple nutrients with potent anticancer properties (Erickson, 2008). Indian mustard is a folk remedy for arthritis, footache, lumbago and rheumatism (Choi and Lee, 2009). The seed is used for tumors in China. Leaves are applied to the forehead to relieve headache (Fitzjohn, 2007). In Korea, the seeds are used for abscesses, colds, lumbago, rheumatism and stomach disorders. Chinese eat the leaves in soups for bladder inflammation and hemorrhage. Mustard oil is used for skin eruptions and ulcers (Maity *et al.*, 2008).

Trigonella foenum

It belongs to the family Fabaceae which is an herb commonly known as venthiya keerai in Tamil and is found in the Mediterranean region. It is grown as a green leafy vegetable and cultivated as semi-arid crop. Due to its estrogen-like properties, fenugreek has been found to lessen the effect of hot flashes and mood fluctuations that are common symptoms of menopause and Pre Menstrual Syndrome (PMS). It is used for the treatment of reproductive disorders, to induce labor, to treat hormonal disorders, lower blood glucose and cholesterol levels, diabetes and CVDs (Grover *et al.*, 2002). Fenugreek seeds are galactagogue that are often used to increase milk supply in lactating women. It is regularly used in balancing cholesterol, treating diabetes, skin inflammation and fever. Its seeds are used in curing numerous diseases like colic flatulence, dysentery, dyspepsia with loss of appetite, diarrhea, chronic cough, dropsy, enlargement of liver and spleen and rickets (Meghwal and Goswami, 2012).

Amaranthus tristis

The leaves of amaranth constitute an inexpensive and rich source of protein, carotenoids, vitamin C and dietary fiber, minerals like calcium, iron, zinc, magnesium and

phosphorus (Shukla *et al.*, 2006). The use of these vegetables in traditional medicine was also reported (Nsimba *et al.*, 2008). It has been reported that *Amaranthus* spp. has high protein contents, with high biological value (Gamel *et al.*, 2005). Amaranth leaves in general are suggested as a good food with medicinal properties for young children, lactating mothers and for patients with fever, haemorrhage, anaemia, constipation or kidney complaints. In Tanzania, the whole plant is used as a medicine against stomachache (Grubbens and Denton, 2004).

Amaranthus polygonoides

The plant *Amaranthus polygonoides* is commonly known as Sirukeerai. *Amaranthus polygonoides* is a species of flowering plant. It has a common name of Tropical Amaranth. This species is valued as a leafy vegetable throughout the South and Southeast Asia and also in Africa (Julkunen, 2009). Its seeds contain large amounts of protein and essential amino acids, such as lysine. This is a common leafy vegetable throughout the tropics and in many warm temperate regions (Cao *et al.*, 2006). It is very popular in India. It is a very good source of vitamins including vitamin K, B6, C, riboflavin and folate and minerals including calcium, iron, magnesium, phosphorus, potassium, zinc, copper and manganese. It is used as an herbal remedy in Traditional African medicine (Vallejo *et al.*, 2008). Regular consumption of Amaranth reduces blood pressure and cholesterol levels, while improving antioxidant status and immunity (Iqbal and Bhangar, 2006).

Sesbania grandiflora

The plant *Sesbania grandiflora* (Fabaceae) is commonly known as “Sesbania” and “Agathi” in ayurvedic system of medicine, agatikeerai in Tamil. It is an open branching tree of fast growing nature. Roots are heavily nodulated with large nodules. The leaves are used as fodder and its seed pods and flowers are used as food. It is well adapted to hot, humid environments and is planted in gardens for its intercropping compatibility and soil improving properties. The young, tender pods are cooked similar to other GLVs. The plant has various uses in folk and traditional medicines for headache, swellings, anemia, bronchitis, pains, liver disorders and tumors. The leaves with various preparations are a potential remedy for bruises, epileptic fits and leprous eruptions (Sreelatha *et al.*, 2011).