

Bioremediation of Dyes and Heavy Metal Ions using Cynodon Dactylon – A Review

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ABSTRACT

The remediation of various Synthetic Dyes like Thymol Blue, Malachite Green, Alizarin Red and Drimarene Dye from waste water as food colorants and Heavy metals like Fluoride ion, Copper ion from the water is studied by researchers using different adsorbents. Recently, the Eco-Friendly adsorbents are playing vital role in adsorbing the hazardous dyes. In this review, the efficiency of Cynodon Dactylon has gained importance due to its Economical value and its ease of availability. The Effect of pH at various concentrations and Temperature has been reviewed.

KEY WORDS: Synthetic dyes, Toxicity, Heavy metal ion, Cynodon Dactylon, pH.

1. INTRODUCTION

Due to increase in the population and the need for industrial development has exploited the natural Resources directly and indirectly. This lead to serious Environmental issues due to the effluent discharge by the various industries directly into the nearby water sources called as Point Source of Pollution. Dye-containing waste effluents, which are generated by several sources like textile, paper, printing, pulp mills, food, cosmetics and leather industries (Djomgoue, 2012; Monvisade, 2009). Among the synthetic dyes nearly 70% of the dyeing industries is composed of azo dye (Mark Daniel, 2013; Gercel, 2008). Most of these dyes are poisonous, mutagenic and carcinogenic (Noureddine Barka, 2011). In addition, it is the largest group of organic dyes that are difficult to degrade even at low concentration due to its high resistant to light, heat, water, chemical and microbial attack (Kornbrust,1985). In addition, dyes have high organic content, non-biodegradable and complex aromatic structure (Hanafiah, 2012). Untreated textile dyeing effluent released from the industries on open land seeps into the underground water table and increases the concentration of pollutants in the groundwater (Iqbal, 2007; Bouyakoub, 2009; Yahya AlDegs, 2008), the heavy metals are non-biodegradable and found to get Bio accumulated in the Food chain. According to the World Health Organization (WHO), among the most toxic metals are copper, cadmium, chromium, mercury, lead and nickel (Ankica Radjenovic, 2005). Various effective methods have been explored to remove the chemical dyes from the effluents (Pragnesh, 2011).

Toxicological Effects of Dyes and Heavy metal ions: Rhodamine (RhB) is mostly used to dye silk, cotton, wool, paper and leather which causes irritation of skin, eyes, respiratory and gastrointestinal tract (Tabrez and Khan, 2013). Thymolsul phone phthalein (Thymol blue) is a reddish-brown or brownish-green crystalline powder that is used as an indicator. It causes several effects to Environment. It transitions from red to yellow at pH 1.2–2.8 and from yellow to blue at pH 8.0–9.6 (Mathubala, 2015). Aquaculture industry uses Malachite green (MG) which is an extensively used biocide (Shivaji Srivastava, 2004). It is also used as a food additive, food coloring agent, a medical disinfectant and as a dye in silk, leather, cotton, paper and acrylic industries (Hameed, 2008). MG has been extensively used as a topical fungicide (Hussein, 1999) and ectoparasiticide in fish farming throughout the world since 1936 (Foster, 1936). Malachite green is not allowed in Germany as an animal drug because of the possible mutagenic, carcinogenic and teratogenic risks for human health. Alizarin Red S (1, 2-dihydroxy-9, 10-anthra- quinone sulfonic acid sodium salt), Alias Mordant Red 3, ARS, is a water- soluble, widely used anthraquinone dye (Samusolomon, 2011). Most of the Azo dyes have proved to be carcinogenic to human and severely affecting other living organisms. The reactive dyes Drimarene can cause allergic dermatoses and respiratory diseases, increased risk of bladder cancer (Kaisa Klemola, 2007; Estlander, 1988).

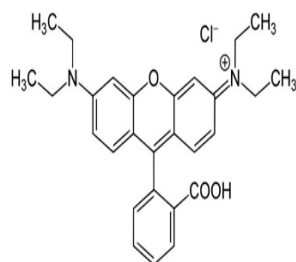


Figure.1. Chemical Structure of Rhodamine B
(Majid Aliabadi, 2012)

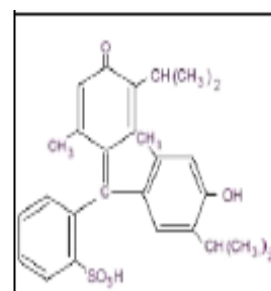


Figure.2. Chemical Structure of Thymol Blue
(Mathubala, 2015)

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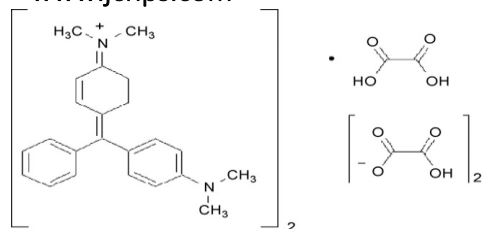


Figure.3. Chemical Structure of Malachite Green (Hussein, 1999)

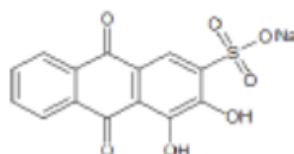


Figure.4. Chemical Structure of Alizarin Red (Samusolomon, 2011)

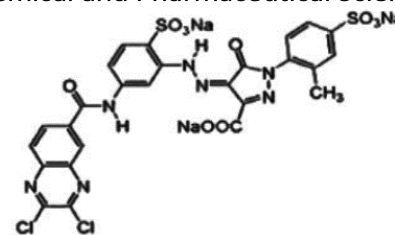


Figure.5. Chemical Structure of Driamerene-K (Ghaly, 2014)

Metal ion and its Toxicity:

Fluoride ion: It is not present in elemental form as it is highly reactive. It exists as fluorides in the common minerals like Fluor apatite, fluorspar, cryolite etc. They are released as pollutants during the manufacture of fertilizers, bricks, ceramics and tiles. In groundwater, natural fluoride concentrations ranges over 25 mg L^{-1} . When humans and other animals inhale fluoride, it is absorbed by body tissues, with long-term deposition in teeth and bones gastrointestinal tract (Susheela, 1993) and also risk of Cancer (Taylor, 1965). During the 1930s, it was discovered that children living near the areas where drinking water with higher concentration of fluoride experienced less tooth decay (Paul, 2005; Hamilton, 1992). In India, the problem of high fluoride concentration of $0.5\text{-}0.8 \mu\text{gml}^{-1}$ in drinking water is having higher incidence of Fluorosis (Sinha, 2000).

Copper ion: Copper has the permissible limit of 0.1 mg/l (WHO-2008). Ingesting large amounts of copper compounds can cause death by nervous system, liver, coronary heart diseases, chronic anemia and high blood pressures although coronary heart ailments have been associated to copper deficiency (Chaitali, 2013) and kidney failure. Minimum concentrations of copper identified for surface, ground water and tap water was 0.020 mg/l with maximum concentration being 0.120 mg/L . Copper ion also inhibits the demineralization of Human Enamel (Brooks, 2003).

Chemistry of Adsorbent (Cynodon Dactylon): Conch Grass is known as dhub, harialil and doob in Hindi names include garikoihallu (Kanarese), durba (Bengali), durva (Marathi), durva or haritali (Sanskrit), arugampullu (Tamil), garikagoddi (Telugu) (Kavya Dashora, 2013). The plant contains carbohydrates, mineral constituents and proteins, oxides of magnesium, Phosphorous, calcium, sodium and potassium. The entire plant contains flavonoids, β -sitosterol, alkaloids, glycosides and triterpenoids (Paranjpe, 2001), vitamin C, palmitic acid, arundoin, selenium, triterpenoids, friedelin, alkaloids- ergonovine and ergonovinine, Ferulic, syringic, p- coumaric, o-hydroxyphenyl acetic acids, vanilic, p- hydroxybenzoic Cyanogenic hyperoside, Cyanogenic glucoside- triglochinin, phenyl acetaldehyde, furfural alcohol, acetic acid, phytol, β - ionone; mono and oligosaccharides, lignin hydrocarbon esters, eicosanoic and docosanoic acids (Amrita Asthana, 2012; Billore KV, 2004). The leaves contain 2-Propanol, 24.37% of 1-hydrazino, 3.45% of Glycerin, 14.90% of n-Hexadecanoic acid, Hexadecanoic acid, 1.83% of ethyl ester, 12.88% of 1-Triacontanol, 9,12- Octadecatrienoic acid (Z,Z), 5.52% of Phytol and 6.68% of Stigmasterol justifying the use of this plant to treat many ailments in folk and herbal medicine (Rawal Jatin, 2016). Cynodon dactylon contain many chemical constituents like Hexadecanoic acid, ethyl ester, Hydroquinone, Linolenic acid, d-mannose (Shabi, 2010). Cynodon dactylon is hardy, perennial grass, with varieties it grow in India ascending up to a height above sea level of 8000feet. It helps in prevention of Soil Erosion (Amrita Asthana, 2012) used as an astringent and is applied to fresh cuts and wounds (Hema, 2013). Hindus worship the God Ganesha with the leaves Durva religiously (Badri Prakash Nagori, 2011). It provides 11.75 percent ash on burning, which has potassium and sodium salts in it. This helps in increasing the number of red blood cells in our body. It helps in maintaining the alkalinity of blood (Kavya Dashora, 2013). Doob Grass possess hypolipidemic properties (Edeh, 2014). Bermuda grass show anti-ulcer activity (Dilpreet Kaur, 2012), Wound Healing Activity (Anand Kumar, 2013), liver function (Kesari, 2007). Used to biosorb heavy metals from the soil (Soleimani, 2009). The Review study is about the adsorption of hazardous dyes and some metal ion using Bermuda Grass.

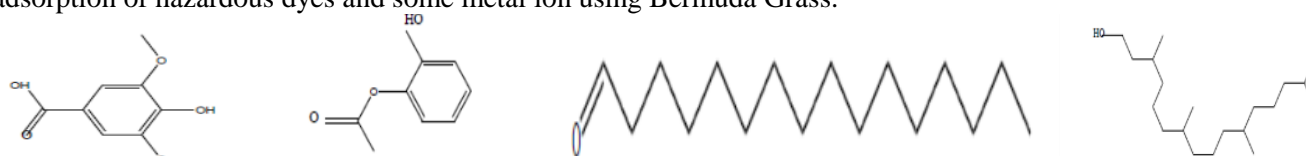


Figure.6. Structure of Syringic Acid, O-Hydroxy Phenyl Acetic Acid, Hexadecanal, Phytol (Amrita Asthana, 2012)

2. MATERIALS AND METHODS

Sorption of Synthetic Dyes and Metal ions using Bio Carbon: Activated carbon is a permeable form of carbon which is mothered from various carbonaceous raw materials like Shell of coconut, pine, wood, Eucalyptus, Coal, peat, Saw dust, Rice husk, Organic food waste, medicinal herbs etc. Due to well-developed pervious structure and large internal surface area, activated carbon has an excellent adsorbent capacity in both forms like fine activated carbon and granular activated carbon. Activated Bio carbon prepared by the various investigators by their different research work have been discussed. Activated bio carbon prepared by treating the leaf powder with the concentrated sulphuric acid and dried at $160\pm 5^{\circ}\text{C}$ of particle size between 90 and 125 micrometer was used to adsorb Thymol Blue and adsorption increased due to the increase in the total area of the adsorbent. The amount of adsorbent for 95% removal of Thymol Blue was 3.5g/100ml (Mathubala, 2015). The activated carbon Black was prepared by the author to remove Malachite green in ratio 1:1. After heating at 600°C for 12 hours the carbon was dried at 125°C and grounded and sieved (Gayathri, 2010). Batch adsorptions were conducted at different concentration to remove different dye by the investigators. Similarly, for Alizarin Red Dye the author had studied the experiments at $25 \pm 1^{\circ}\text{C}$. Also the adsorbent was free from High moisture content and volatile matter. The mesh size 0-200 microns were used to adsorb the dye. As the mesh size is larger, the size of the particle is decreased which results in more surface area. The maximum removal was 88.75% at 25 ppm. The minimum adsorption was 97% at 30°C and maximum was 96% at 60°C for 25ppm of the solution. 0.6g of adsorbent is used for dye concentration 25ppm at 30°C at pH 1.0 (Samusolomon, 2011). The activated carbon was prepared by drying the grass at 105°C and treated with 7% HCl to remove Drimarene dye by the author. The particle size of mesh size 0-63, 63-125, 125-250 was studied by the author. 0.5g of adsorbent with 50ml of different concentration of dye at different temperature 30, 45 and 60°C was studied by the investigator. The dye adsorption increased with increase in temperature from 30 to 60°C of dye concentration 10-60 ppm due to attainment of equilibrium at low temperature (Mohammad Sajid Ansari, 2013). The adsorbent was dried in muffle furnace at 1073K and particle size of less than 53, 53-106, 225-305 mesh was used by the investigator to adsorb Fluoride ion. Batch adsorption was done by mixing 1.25g of adsorbent and studied at 303 K. The adsorption increased with time and at 105 min it attained equilibrium. The sample with 53 μm registered high defluoridation efficiency due to larger surface area (Ganapathy alagumuthu, 2011). To adsorb Copper ion from the water the adsorbent was prepared by treating with conc. Sulphuric acid in a weight ratio 1:1, and dried in a furnace maintained at 600°C for 12 h. Then dried for 5 hr at $120\pm 5^{\circ}\text{C}$. The carbon products between 0.022-0.025 mm sieves were separated. For entire adsorption studies 25 mg/50 mL of dosage of adsorbent was found to be enough (Amrita Asthana, 2012).

Effect of pH: The investigator depicts the adsorption of Thymol Blue on the carbon at various pH levels is given in figure.7. Thymol Blue was found to be adsorbed in a pH of 3 to 5. Adsorption decreases below pH 3 and above pH 5. The percentage removal of Thymol Blue in the synthetic waste water system was 95% with the effective bio carbon load of 3.5 gm/ 100ml of the sample (Mathubala, 2015). Adsorption of Malachite Green was carried by the author at pH 3-9 is shown in the Fig.6. The adsorption increased from 34-90%. The dye removal was achieved using 0.025g of carbon (Gayathri, 2010). At pH range 1-5 the percentage of Alizarin Red S adsorption was studied. The results obtained are shown in Fig.8. The minimum adsorption was 0% at pH 5.0 and maximum adsorption was 97% at pH 1.0 for 25 ppm initial concentration of dye Solution (Samusolomon, 2011). The maximum adsorption of Drimarene dye (42.5%) was observed at pH 7.0 from dye solution having 40 ppm concentration. The minimum adsorption (15%) was observed at pH 1.0 from the same dye solution (Fig.9). This decrease in adsorption may be attributed to weakening of electrostatic force of attraction between the oppositely charged adsorb ate (Mohammad Sajid Ansari, 2013). In the Fluoride ion removal it was revealed by the author that 83.77% of fluoride is removed at neutral pH (Ganapathy Alagumuthu, 2011). The copper ion removal was found at pH range 3-10 (Fig.10). This indicates the strong force of interaction between the copper ion and the activated Carbon. Here the interaction is more at pH 5.5, the competence of acidic H^+ ion with copper cation for the sorption sites. The adsorption of copper ion involve ion exchange mechanism (Gayathri, 2011).

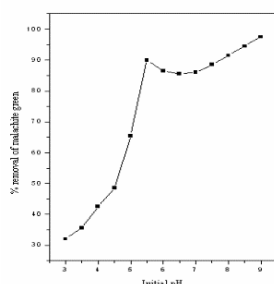


Figure.6. Effect of pH of Malachite Green (Gayathri, 2010)

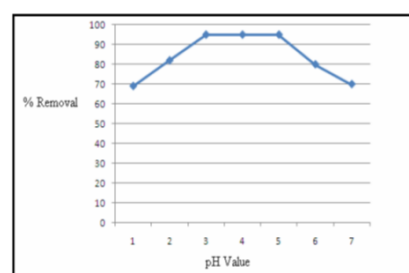


Figure.7. Effect of pH of Thymol Blue (Mathubala, 2015)

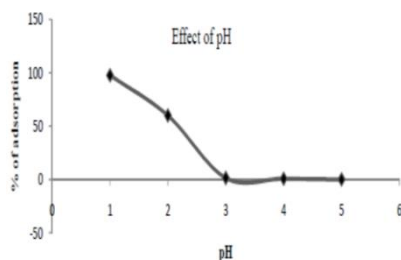


Figure.8. Effect of pH of Alizarin Red Dye (Samusolomon, 2011)

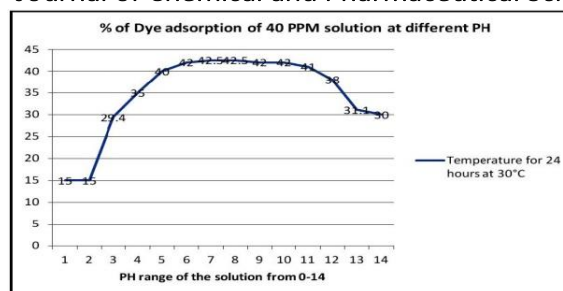


Figure.9. pH effect of Drimarene Dye (Mohammad Sajid Ansari, 2013)

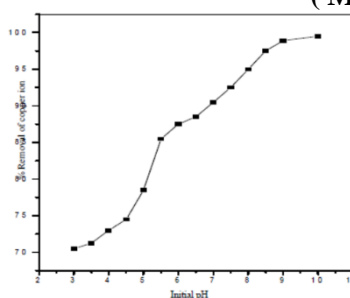


Figure.10. pH effect of Copper ion (Gayathri, 2011)

Adsorption isotherm:

Langmuir Isotherm: The Langmuir isotherm for the surface with finite number of identical site called the Monolayer sorption, the Equation is given by

$$q_e = \frac{a_L b_L C_e}{1 + b_L C_e}$$

For solid liquid systems, the Linear form of Langmuir isotherm is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b_L} + \frac{C_e}{Q_{\max}}$$

Where, Q_{\max} = monolayer adsorption capacity, ($\text{mg}\cdot\text{g}^{-1}$), signifies the solid phase concentration, corresponding to the complete coverage of available sorption site, can be evaluated from the slope of Langmuir isotherm plot (C_e/q_e against C_e), b_L = Langmuir Isotherm constant, ($\text{L}\cdot\text{g}^{-1}$). This value corresponds to energy of sorption, calculated from the intercept of the linear plot of Langmuir isotherm. The influence of the isotherm shape for 'favorable' and 'unfavorable' sorption, on the basis of feasibility criteria, was studied by Weber and Chakraborti. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L , which describe the type of isotherms and is defined by,

$$R_L = \frac{1}{1 + b \cdot C_0}$$

Where, b is Langmuir constant introduced in equation and C_0 is the initial concentration.

Freundlich Isotherm: The freundlich isotherm model is derived by assuming a heterogeneous surface of heat of adsorption over the surface, the Freundlich model is non-linear & linear form can be expressed as

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

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where, K_F is the freundlich characteristics constants and $1/n$ the heterogeneity factor of adsorption, obtained from intercept and slope of $\ln(q_e)$ vs $\ln(C_e)$ linear plot respectively.

For Alizarin Red Dye, The K_1 value for the Langmuir isotherm, Fig.11, 16.32mg/g indicated the high adsorption capacity of biosorbent toward alizarin adsorption. The correlation coefficient value calculated for the Freundlich isotherm, Fig.12, was found to be 0.993 (Samusolomon, 2011).The research worker suggests for the malachite green dye, formation of monolayer of adsorbate on outer surface of adsorbent obeys Langmuir adsorption, Fig.14, and Freundlich adsorption, Fig.13, showed surface heterogeneity of the adsorbents. The high value of adsorption co-efficient greater than 95% showed adsorption of malachite green dye (Gayathri, 2010).The investigator reveals for Fluoride ion, the average monolayer adsorption capacity, Q_m , is 4.702 mg/g, Fig.16. However, the Freundlich isotherm model, Fig.15, based on multilayer adsorption, describe the Freundlich coefficient, n , values

ranging from 1 to 10, is high as 5.0–6.3, and that supports the favorable adsorption of fluoride onto the adsorbent (Ganapathy Alagumuthu, 2011). For copper metal ions the author reveals, the Linear plots of $\log Q_e$ shows Freundlich Isotherm, Fig.17, (Gayathri, 2011) also the value of n between 2 to 10 shows good Multilayer adsorption, Fig.18 (Gayathri, 2011).

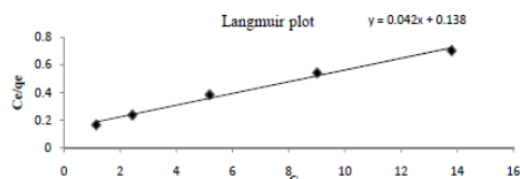


Figure.11. Langmuir isotherm for Alizarin Red (Samusolomon, 2011)

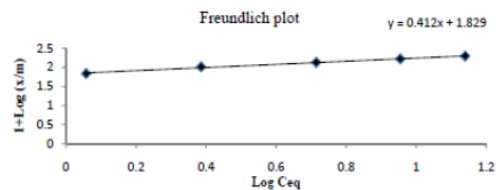


Figure.12. Freundlich isotherm for Alizarin Red (Samusolomon, 2011)

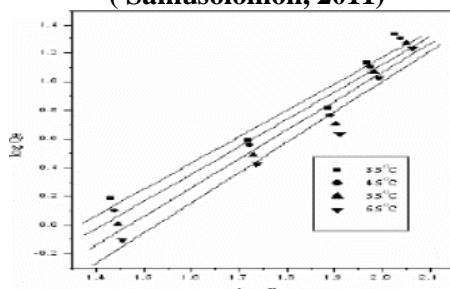


Figure.13. Freundlich isotherm of Malachite green (Gayathri, 2010)

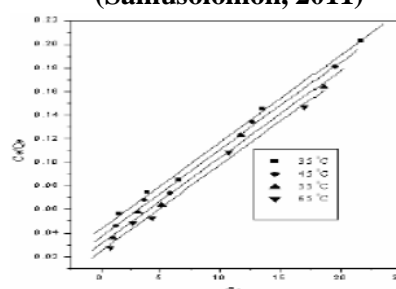


Figure.14. Langmuir isotherm of Malachite green (Gayathri, 2010)

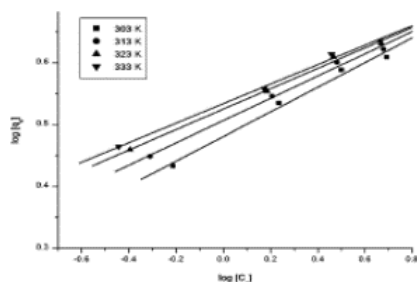


Figure.15. Freundlich isotherm of Fluoride metal ion (Ganapathy alagumuthu, 2011)

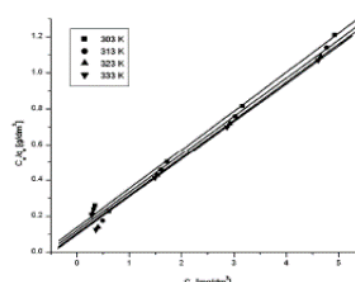


Figure.16. Langmuir isotherm of Fluoride metal ion (Ganapathy alagumuthu, 2011)

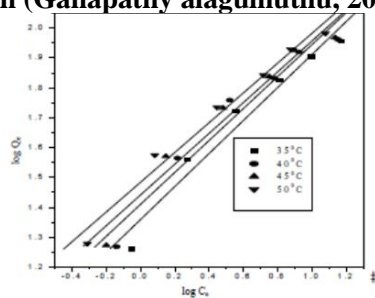


Figure.17. Freundlich isotherm of Copper metal ion (Gayathri, 2011)

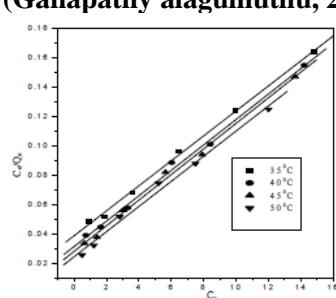


Figure.18. Langmuir isotherm of Copper metal ion (Gayathri, 2011)

Thermodynamic parameters: The adsorption process in the solution is calculated using the parameters for the adsorption process in solution have been calculated using the following standard thermodynamic relations:

$$\Delta G = -RT \ln K$$

Where ΔG is the standard free energy change (kJ/mol), T is the temperature (K) and R is universal constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). K denotes the distribution coefficient for the adsorption. The negative value of the $-G^\circ$ at the studied temperature range indicated that the sorption of alizarin Red S on sorbent was thermodynamically feasible and spontaneous. The increase in the value of $-G^\circ$ with temperature further showed the increase in feasibility of sorption at the elevated temperature for cynodon dactylon (Samusolomon, 2011). The positive values of standard enthalpy change and standard entropy change indicates endothermic reaction for the study of malachite green dye. Also the ΔG° value shows the adsorption is spontaneous and the positive value of ΔS° showed the increased randomness (Gayathri, 2010; 2011; Ganapathy Alagumuthu, 2011).

3. CONCLUSION

On account of the Research investigators, the adsorption was done by environment friendly, cheaper and easy availability of the conch grass. Its medical values are wider. The hazardous metals and the synthetic food dyes effluents can be treated by this grass as active carbon. Various investigators have studied the efficiency of Durva grass and few of it has been reviewed above.

4. ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to our Honorable Chairman, Dr.K. Ramakrishnan for his motivation and kind support to us in doing research. My sincere thanks to our Distinguished Executive Director, Dr.S. Kuppusamy for his continuous encouragement in research activities. I extend my Duty bound gratitude to our Esteemed Principal, for guiding me with his vast experience of knowledge and giving valuable ideas in research and is always the well-wisher and inspiration for us. Also I am Thankful to my Department Head and Colleagues.

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