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ADSORPTION OF TEXTILE DYES BY PLANT BIOMASS-A REVIEW

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ABSTRACT

Water resources are increasingly getting contaminated day by day due to the ignorance lent to the wastewater management.Most of the textile dyes or effluents are a major reason for the pollution of water resources.Although many methods are adopted to treat these textile effluents,but there is a dire need to come up with an eco-friendly,cost effective method for the removal of contaminants from the effluents. Recent researches have shown that plant biomass can be used for this purpose. Different plant parts can be put to use for the removal of textile dyes from wastewater and make the water cleaner for various uses.This is an economical and environment friendly alternative to various other methods that use large amount of chemicals to treat waste water.Different plants like water hyacinth,nirgudi plant,hydrilla verticillata,sunflowers,etc have been researched upon for the adsorption of textile dyes from textile wastewater.

Keywords: Biosorption, Wastewater, Adsorption, Phytoremediation, Contaminants

I. INTRODUCTION

Textile industries are one the main industries in the world that extensively contribute to the country's economy in terms of employment generation,industrial output and foreign exchange earnings. But, the textile industry is also a major reason for water pollution.The textile industries discharge a huge amount of dyes in water that are difficult to remove with the treatments that these effluents undergo before being discharged into water bodies. Around 10-25% of the total dyes used are lost during the dyeing process, another 2-20% are directly discharged as aqueous effluents into the water bodies.[1]This issue has led to various problems such as adversely affecting the flora and fauna.The breakdown products of textile dyes such as benzidine,naphthalene and other aromatic compounds are extremely difficult to decompose and can stay in the environment for a very long time.Many methods are adopted to treat the textile wastewater.Due to the differing chemical compositions and stability of the textile dyes,different methods are used for the treatment of different dyes in textile effluents.These effluent treatment methods are classified in three categories,namely, physical,chemical and biological methods.However, these treatments have proved to be insufficient for the treatment of textile dyes.By combining the treatment methods,around 85% of the wastewater effluents can be removed.[1].But the resulting effluent is usually high in colour. Hence in order to get better results in a cost efficient way,different methods are being adopted for wastewater treatment.The traditional treatment processess like physical and chemical methods such as flocculation,coagulation,adsorption,membrane filteration and irradiation have two major drawbacks-:high cost and production of significant amount of sludge that requires final disposal again.[2]

The adsorption process was considered to be a very useful alternative for the traditional methods of wastewater management.Granular activated carbon which was used for the purpose gave satisfying results,but the whole process was very expensive.[2]Hence,a more cost efficient and environment friendly method was found out.Biosorption is the process that used living and non-living biomass is used to adsorb textile dyes from the effluent discharged by the textile industries.[3]This has proved to be an effective method as compared to other traditional methods which is cost efficient and effective in adsorbing dyes from textile wastewater.In this review,an overview of different plant materials has been provided that have been researched to remove dye contamination from textile effluents.

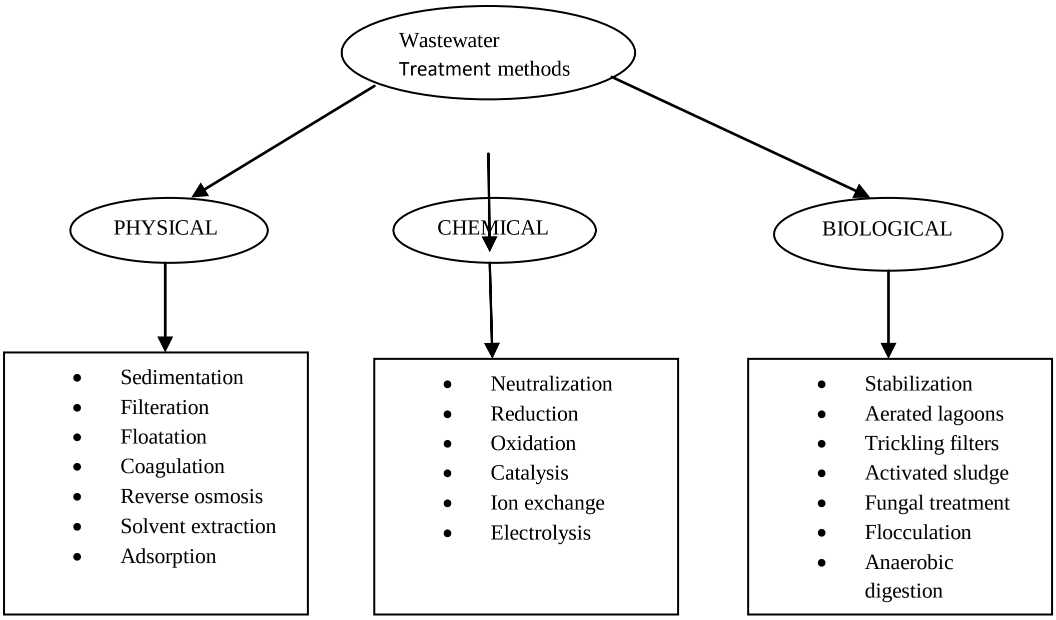

Fig.1: Various Methods of Wastewater Treatment

II. TEXTILE WASTEWATER TREATMENT METHODS

2.1 Coaggulation/Flocculation

The addition of coagulant chemicals to primary clarifiers, or to other dedicated physical separation processes, is an effective way of reducing the load to downstream biological processes, or in some cases for direct discharge. This practice is generally referred to as chemically enhanced primary treatment, or CEPT. Coagulation has been defined as the addition of a positively charged ion such as Al^{3+}, Fe^{3+} or catalytic polyelectrolyte that results in particle destabilization and charge neutralization. The purpose of coagulation is removal of finely divided suspended solids and colloidal material from the waste liquid[5].

Flocculation is the formation of clumps or flocs of suspended solids by agglomeration of smaller suspended particles. Most chemical precipitates do not possess the property of flocculation to any appreciable degree, but rather tend to form dense, compact, crystalline particles that settle rapidly. Precipitates of ferric hydroxide, aluminum hydroxide, silica, and certain other substances formed by chemical reaction of coagulant chemicals, however, have the property of forming large flocs of high surface area[5]. As these flocs move through the liquid in a settling tank, they remove other suspended solids by adsorption or mechanical sweeping, and hence perform a better clarification than could be achieved by plain sedimentation alone.

A major disadvantage of this technique is its operational cost. Sometimes, considerable amount of coagulants and flocculants are used to achieve the required level of results.A certain quantity of physic-chemical sludge is also formed, which is normally processed externally.This can increase the costs for large volumes of wastewater.

2.2 Membrane Filteration

There are two classes of membrane process used in the water and wastewater field. The first category includes reverse osmosis (RO) and nanofiltration (NF). These membranes have a dense non porous separating layer cast onto a porous support, and are used for the removal of dissolved substances[4]. The second category is membrane filtration, in which a micro-porous separating layer provides a barrier to the finest particles present in the feed source but allows dissolved components to pass through. Membrane filtration is often used as a treatment process in its own right, but may also be used as pre-treatment to an RO stage.With time, the solute or particles deposit onto the membrane.These deposits can adversely affect the water generated and reduce the efficiency of the filteration.Hence, these membranes have to be changed from time to time.This increases the operational costs of the process.

2.3 Irradiation

One of the techniques that have been recently implemented in several countries is the utilization of ionizing radiation for wastewater and industrial wastes treatment[4]. High power accelerators are used as well-controlled sources for radiation treatment of wastewater. The radiation treatment of sewage sludge offers an efficient, simple and reliable method to produce pathogen-free sludge, which can be further upgraded to produce bio-fertilizers.Effluents samples were collected at the urban wastewater treatment station of Tetouan and were irradiated at different doses ranging from 0 to 14 kGy using a Co^{60} gamma source. The results showed an elimination of bacterial flora, a decrease of biochemical and chemical oxygen demand, and higher conservation of nutritious elements. The results of this study indicated that gamma irradiation might be a good choice for the reuse of wastewater for agricultural activities[4]. Various other radiations can be used for the purpose-:uv radiation, ultrasonic radiations.

The main disadvantage of irradiation process is that it is not cost effective.Low dosage of radiations may not work well with the wastewater treatment.

2.4 Adsorption

A wide range of adsorbents (granulated as well as finely powdered) including activated carbon, clays, bentonite, fly ash, alumina, magnesium oxide , ferric oxide, silica, saw dust, zeolites, and activated anthracite volcanic ash soils are used in waste water treatment for the removal of heavy metals and dyes which result in the reduction of COD,BOD and colour[3]. Activated carbon is an excellent adsorbent because it has a strong affinity for binding organic substances, even at low concentration. It has a vast network of pores of varying size to accept both large and small contaminant molecules and these pores give activated carbon a very large surface area.

III. EFFICIENT METHOD TO REMOVE DYES FROM WASTEWATER-BIOSORPTION

Wide variety of synthetic dyes are used in textile industries, paper industries, colour photography, pharmaceuticals, food, cosmetics and many other industries.The class of the dye plays an important role in determining the amount of dye lost in effluent. For example,only 2% dyes are lost when basic dyes are used, but 50% dyes are lost when reactive dyes are used[5]. Adsorption of wastewater dyes by plant material or biomass is an emerging and eco-friendly process for removal of textile dyes as well as heavy metals present in industrial effluents.Research studies reflect the potential of various plant materials or biomass for considerable amount of removal of textile dyes from the wastewater.

3.1 Water Hyacinth

Water hyacinth is one of the worst growing weeds.It is detrimental to the aquatic flora as it intervenes with the photosynthetic activity of the aquatic plants because it absorbs the sunlight that falls on the water surface.Many researches have been performed to test the ability of water hyacinth to absorb aqueous dyes in water.It was observed that biomass of non-living, dried roots of water hyacinth can remove Methylene Blue[2] and Victoria Blue[6] from their aqueous solutions.The study focused on the following parameters-pH, sorbent dosage, contact time, initial concentration.The sorption data was represented by Langmuir isotherm.The maximum sorption capacity was noted to be 128.8 mg/g for methylene blue and 145.4 mg/g for Victoria Blue[6]. The result prove that water hyancinth is an effective adsorbent for removal of dyes.

3.2 Nirgudi Plant

Nirgudi plant is commonly found in Maharashtra and is used as a natural fence. Nirgudi is believed to have curative properties.This plant can grow without much water and manure, and is highly sustainable.Various batch processes were conducted focusing on using nirgudi plant mass to adsorb acid dyes[7].Acid treated nirgudi leaf powder was used to adsorb acid blue,acid red and malachite green from its aqueous solutions.According to a study that used stock solutions of dyes (1.0 x10^{-3}M) in double distilled water,the dye solutions were treated for 60 min in glass tubes with acid treated nirgudi leaf powder.After treatment,the concentration of dye solution was calculated by spectroscopy at their respective wavelength,i.e., Acid blue (λmax = 664nm) Acid Red (λmax = 548) and for Malachite Green (λmax = 616nm). ΔG_0 was calculated to be -15KJ that indicated physical adsorption[7]. The calculated dimensionless equilibrium parameter RL found to be in the range between 0 to 1 is indicative of favourable adsorption onto the surface on the adsorbent.Results prove that the process was first order kinetic process with low activation energy[7].

3.4 Indian Mustard

Indian Mustard (*brassica juncea*) was subject to many experiments involving the removal of high tissue concentrations of lead in soil[8].EDTA was added to Indian mustard to improve the results.By providing an electric field around the plants increased the uptake of lead showing better results[8].In a related research, bench scale studies illustrated the application of electrodic phytoremediation with EDTA for lead using Indian mustard. Various parameters such as operating current/voltage with different concentrations, application time of EDTA and electric potential, and daily application time of electric potential were studied and used to check the capability of Indian mustard to remove lead. The maximum lead accumulation in the shoots was obtained with the application of electric field 1 h per day for 9 days with EDTA[8].

3.5 Hydrilla Verticillata

Hydrilla is a profusely branching perennial plant that forms dense colonies and can grow to the surface in water over 20 feet deep.A study was based on Hydrilla Verticillata Casp,[9] wherein, 100gms of hydrilla was cultured in a plastic tub of 20 litres capacity containing domestic wastewater,for about a week. The second one was left without aquatic plant but filled with municipal wastewater, used as control.After an year, after the required experiments, water samples were collected in plastic bottles that were soaked in 10% nitric acid for 24 hours and rinsed with double distilled water[9]. Hydrilla Verticillata is known to adsorb malachite green[10].The research was conducted with malachite green. To each 100 mL solution of Malachite green, a desired quantity of the Hydrilla verticillata biomass was added in 250mL Erlenmeyer flasks. The mixture was agitated in an incubated orbital shaker at the desired temperature and desired speed for predetermined time intervals. The supernatant was agitated by centrifugation at 4000 rpm for 10 min. The maximum adsorption capacity was obtained (91.97 mg/g) at a solution pH ~8.0. From the kinetic and equilibrium studies it was found that pseudo II order kinetics and Freundlich isotherm fits the data well respectively[10].

3.6 Sunflower

Sunflower or helianthus plant parts have also been actively researched upon for removal of echans blue[11][12].20 mg/l of dye solution was studied with living leaves, stems and roots of sunflower plant. The decolorization capacity after 31 hours was observed to be 48.7%, 47.7% and 40.6% with living leaves, stems and roots respectively[11]. The results when obtained with dead leaves,stem and roots was noted to be 14.2%, 20.2% and 14.1% respectively [11].The results obtained at different concentrations were similar to that when obtained with 20 mg/l. The results show that decolorization of Evans blue by tissues of sunflowers was partly attribute to degradation and partly due to sorption. Plant root has large root surface area that provides a good adsorption media. In average, biosorption of roots accounted for 33.3% of the total dye removal during 31 hours[11].

3.7 Corn Cob

Corn cobs are an essential part of biofuels, mild abrasive for cleaning building surfaces, charcoal production, etc. Corn cob is seen as an efficient adsorbent for the removal of malachite green[13][14][16][17]. Batch studies were carried out using an orbital shaker which rotated at a constant speed of 120 rpm maintained at 30^0c using 250 ml conical flask [17]. 10 ml of dye was reacted with 50 ml of adsorbent and after certain time intervals, mixture was withdrawn from the flask. The adsorbent was centrifuged at 6000 rpm for 5 min and the dye concentration was determined by spectroscopy using Ellico make UV visible spectrophotometer at λ max =617nm[17]. It was observed that with the increase in adsorbent dosage and increasing initial concentration the percentage colour removal increases. Optimum contact time for equilibrium to be achieved is found to be 100 min. For malachite green maximum adsorption found to be at pH = 12.The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH[17].

3.8 Leaf Biomass

Leaf biomass is a potential adsorbent for different dyes present in wastewater of textile industries[15].Due to the porous structures of the leaves,they can adsorb dye molecules effectively.The functional groups on the leaves can attract ionic dye molecules of opposite charge which lead to increase in dye removal efficiency. Gulmohar(*deloxia regia*) has been studied as an adsorbent for the removal of Methylene blue from aqueous solution[19].The materials were studied without chemical treatment.The adsorption showed best results at higher pH and lower temperature.The equilibrium data were well fitted by the Langmuir isotherm an appreciable Langmuir capacity of 0.3 mg/g was found out.

A Phoenix tree leaf has also been researched for the adsorption of methylene blue from the aqueous solution[18][19].The leaves contain abundant floristic fiber,protein and some functional groups such as carboxyl, hydroxyl and amidogen,etc.The adsorption capacity of phoenix leaves is 80.90, 83.80, 89.70 mg/g at 295, 305 and 323 K, respectively, makes it an adsorbent of little importance for dye removal[18].

Neem leaf has shown excellent results in the removal of Remazol Blue RR dye from aqueous solution[19][20].Pine apple leaf powder has been recently studied to remove Methylene Blue from aqueous solution[21].Pine apple leaf powder is a complex material containing 70-80% cellulose, 5-10% lignin and hemicelluloses. The maximum adsorption capacity varied from 4.68×10^{-4} to 9.28×10^{-4} mol/g when pH increases from 3.5 to 9.5[21].The capacity increased as the initial Methylene blue concentration increases. The adsorption increases with decreasing temperature suggesting that the adsorption reaction is exothermic in nature.

The table given below shows a summary of different plants that are known to adsorb various dyes.

PLANTS	*DYE ADSORBED*	*REFERENCES*
Water Hyacinth Roots	Methylene Blue,Victoria Blue	[2],[6]
Nirgudi Leaf Powder	Acid Blue,Acid Red, Malachite Green	[7]
Indian Mustard	Lead extracts in soil	[8],[12]
Hydrilla Verticillata	Malachite Green	[9],[10]
Sunflower	Evans Blue	[11],[12]
Corn Cob	Malachite Green	[13],[14],[16],[17]
Gulmohar	Methylene Blue	[19]
Pheonix Tree Leaf	Methylene Blue	[18],[19]
Neem Leaf	Remazol Blue RR	[19],[20]

Table 1: Adsorption of dyes by plant materials

IV. FACTORS AFFECTING ADSORPTION

There are various factors that affect the adsorption rate of a reaction.In this review we discuss about the effect of initial dye concentration, effect of pH, effect of adsorbent dosage, effect of contact time, effect of agitation speed and temperature[15].

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4.1. Effect of Initial Dye Concentration

Since a given mass of sorbent material can adsorb a fixed amount of dye , hence experiments with different concentrations of dyes gives different results[1].The effect of initial dye concentration can be carried out by preparing adsorbent-adsorbate solution with fixed adsorbent dose and different initial dye concentration for different time intervals and shaken until equilibrium[15].Normally it is observed that the dye removal efficiency decreases with increase in initial concentration of dye.The amount of dye that can be adsorbed for a given mass of adsorbent is fixed. The higher the concentration of dye , the smaller the volume is removed. At a low concentration, many unoccupied active sites on the adsorbent surface are present, and when the initial dye concentration increases, the active sites required for adsorption of dyes will be lacking.According to some researches, with the increase in initial concentration, the time taken to attain equilibrium also increases.But the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration[3]. This may be due to the high driving force for mass transfer at a high initial dye concentration.Hence, the adsorption is highly effected by the initial concentration of dyes.With increasing concentration, the available adsorption sites become fewer which in turn reduce the percent removal of dyes from aqueous solutions.

4.2 Effect of pH

pH of a solution is a measure of acidity (pH<7) or basicity (pH>7) of that aqueous solution.The pH of a medium is an important factor as it will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules[3].The pH of the dye solution can be adjusted by the addition of dilute 0.1N HCl or 0.1N NaOH. Usually, the percentage of dye adsorption is more for cationic dyes at higher pH, whereas dye removal is less in case of anionic dyes at higher pH[2]. On the other hand, when the pH is low, anionic dyes show better results than cationic dyes. At lower pH, adsorption is less in case of cationic dyes due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in solution pH, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption. With an increase in the solution pH, the electrostatic repulsion between the positively charged cationic dyes and the surface of adsorbent is lowered and consequently the removal efficiency is increased.

4.3 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption process can be carried out by preparing adsorbent-adsorbate solution with different amounts of adsorbents added to fixed initial concentration of dye and shaken together until equilibrium time[15]. It has been observed that the percentage of dye removal increases with an increase in adsorbent amount.Initially, the amount of adsorption is rapid, but as the dosage increases, the removal percentage slows down[2][3].This is because at lower adsorbent dose, the adsorbate is more easily accessible, thereby increasing the removal of dye per unit weight.But after a certain dosage the increase in removal efficiency is insignificant with respect to increase in dose because at higher adsorbent concentration there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when adsorbent dose is lower.

4.4 Effect of Contact Time

The effect of contact time on adsorption process can be carried out by preparing adsorbent-adsorbate solution with fixed adsorbent dose and initial dye concentration for different time intervals and shaken until equilibrium.Generally, the percentage of dye adsorption increases with increase in contact time upto a certain extent.After this point,due to the lack of available adsorption sites, the percentage removal of dye is not affected[5][1]. At this point, the amount of dye desorbing from the adsorbent is in the state of dynamic equilibrium with the amount of the dye being adsorbed onto the adsorbent. The time required to attain the state of equilibrium is known as equilibrium time, and the amount of dye adsorbed at the equilibrium time is the maximum adsorption capacity of the adsorbent under those specified conditions.

4.5 Effect of Agitation Speed

In batch adsorption systems, different results can be obtained by differing the agitation speed of the adsorbent–adsorbent solution[7][8].The effect of agitation speed on adsorption of dye can be carried out by changing the speed of rotation of adsorbate-adsorbent solution keeping other parameters constant.Increasing the agitation speed decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface[12]. Due to this, the adsorption is increased and the percentage removal of dye increases with increase in agitation speed.

4.6 Effect of Temperature

Temperature indicates whether the adsorption process is exothermic or endothermic. If the adsorption capacity increases with increasing temperature then the adsorption is an endothermic process[12][9].This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature.Increasing temperature may decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing adsorption capacity.

V. CONCLUSION

In this review, many studies regarding low-cost adsorbents have been mentioned. These adsorbents can be widely used in order to treat the textile industry effluents. Various plants used in these processes grow in abundance and the processes involved are cost efficient, thereby making biosorption an attractive alternative to various traditional methods of dye removal. The plant biomass can be chemically treated before using them as adsorbents in order to increase their adsorption capacitites. This budding technology is applicable to a broad range of contaminants, including metals and radionuclides, as well as organic compounds like chlorinated solvents, polycyclic aromatic hydrocarbons, pesticides, explosives, and surfactants. Since removal of dyes from textile wastewater by plant material is a new technology, hence various advancements can be applied to this technology to make it more efficient, eco-friendly and cost- effective.

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