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Various Methods for Removal of Dyes from Industrial Effluents - A Review

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Abstract

Objectives: To explore most suitable and efficient method for the removal of dyes from textile effluent. **Methods/ Statistical Analysis:** In this paper, scattered information of research work carried out by many researchers related to various methods for the removal of cationic dyes especially Rhodamine-B, Methylene Blue, Crystal Violet, Malachite Green and Safranin-O dye present in textile effluent have been compiled and compared to find out cheap and effective method by calculating their percentage removal. **Findings/Recommendations:** It has been found that among all the methods reported so far, Adsorption process show promising results and overcomes almost all the demerits of otherwise efficient methods like advanced oxidation and electro coagulation etc. in terms of high cost and sludge problem. So ,the use of natural adsorbents and agricultural/industrial waste materials especially modified flyash, red mud ,activated rice husk , surfactant modified alumina, bentonite clay as adsorbents is recommended for the removal of cationic dyes since they are of less cost/ no cost, easily available and have great affinity for dyes. Moreover, agriculture/industrial waste often poses a disposal problem. So, their use (after chemical treatment) as adsorbent is environmental friendly. **Applications/Improvements:** This review paper would be helpful to find the most promising method for the removal of cationic dyes from the textile effluent considering the merits and demerits of each method. Much work has been done to explore the most effective and cheap method for the removal of dyes recently but not under the range of operating conditions. In future, more methods need to be explored to study and check removal of dyes from real textile effluent at the industrial level as the dye effluent also contains other harmful pollutants. Attention is to be paid to develop cheaper and more efficient adsorbents from the agriculture/ industrial waste with some modification which would be cost effective. Moreover, management of exhausted adsorbents is also to be taken care of.

Keywords: Biodegradable, Biosorbent, Cationic Dyes, Carcinogenic, Solvent Extraction and Fenton's Reagent

1. Introduction

Textile manufacturing is one of the ever developing industrial areas that discharge heavy loaded chemicals during dyeing process that leads to special environment concern. Huge amount of water has been consumed by textile industry that at the last discharged off, fully loaded with organic pollutants, acid, bases, heavy metal ions and dyes etc.[1] Textile industry has replaced natural colouring pigments (used earlier) with new fast colouring agents as they last longer even if exposed to heat, light, water, providing bright colours, but they contribute a lot to water pollution.[2]

Dyes are basically organic compounds that get attached to the surface of the fabric to impart color, commonly known as coloring agents. They are water soluble, producing bright colors in water with acidic properties. Dyes are widely used in many industries that include paper, printing, textile, food, cosmetic and many others. Researchers rose to formulate new color compounds that would impart permanent bright color to the fabric but, these chemicals and their breakdown products are highly

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toxic and carcinogenic. Moreover, they resist to aerobic biodegradation, causing challenge to the environmental researchers. They remain in the environment for long time period hence decreases the aesthetic value of water bodies along with environment hazards.[3] Figure 1 shows the schematic representation of the effects of textile effluents when discharged into the environment.

Figure 1. Schematic representation of the effects of textile effluents when discharged into the environment.

The dyes used in the Textile industry are classified as such-[4]

1. Cationic dyes- include basic dyes.
2. Anionic dyes- include acid dyes, reactive dyes, azo dyes, direct dyes.
3. Non-ionic dyes- includes disperse dyes that do not ionize in aqueous media.

Table 1 represents the details of some target dyes considered for present study.

Most current techniques used for the removal of dyes falls under three main classes-[5]

1. Physical methods (includes process of adsorption involving natural adsorbents, agricultural and industrial adsorbents, surfactants.)
2. Chemical methods (includes advanced oxidation method using Fenton's reagent, hydrogen peroxide, ozonization, solvent-extraction method andelectro-coagulation etc.)

Table 1. Represents the details of some target dyes considered for present study

Name of the dye	type	appearance	Molecular formula	IUPAC name	Health hazard	Reference
Rhodamine B	cationic	Red to violet powder	$C_{28}H_{31}ClN_2O_3$	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride	Carcinogenic and teratogenic	In[108]
Methylene Blue	cationic	blue	$C_{16}H_{18}ClN_3S$	3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride	Serotonin syndrome, jaundice, shock, vomiting, red blood cell breakdown, allergic reactions	In[125]
Crystal violet	cationic	Blue-violet	$C_{25}H_{30}ClN_3$	Tris(4-(dimethylamino)phenyl) methylium	Mitotic poison, potent carcinogen and clastogene promoting growth of tumour.	In[123]
Malachite Green	Cationic	Green crystalline powder	$C_{23}H_{25}ClN_2$	[4-[4-(dimethylamino) phenyl]-phenylmethylidene] cyclohexa-2,5-dien-1-ylidene]-dimethylazanium	Extreme irritant, moderate toxicity, have adverse effect on brain, kidney, nervous and respiratory system	In[113]
Safranin-O	cationic	Green metallic lustre	$C_{20}H_{19}ClN_4$	3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride	Eye and skin irritant respiratory problems,	In[134]

3. Biological methods (includes use of algae, bacteria and fungi species)

2. Chemical Methods for Dye Removal

2.1 Advanced Oxidation Process

Advanced oxidation method is one of the traditional methods that have been applied for de-colorization process. It is based on the mechanism involving generation of hydroxyl radicals (as oxidising agents), that when attack upon chromo-genic groups, leads to produce organic peroxide radicals and ultimately transform them into CO_2, H_20 and inorganic salts.[6] It consists of a variety of methods such as ozonisation, use of hydrogen peroxide and Fenton's process that has been discussed here.[6]

2.2 Using Hydrogen Peroxide

Hydrogen peroxide has attained prominent position among oxidising agents because of its commercial availability and is cheap and friendly oxidant. It can be used for the oxidation process directly or in combination with catalysts or with UV radiation.[7,8] H_2O_2 readily undergoes reaction with hydrated electron from the water radiolysis reaction, that leads to formation of OH* radical.

$$H_2O_2 \quad + \quad e^-_{aq} \quad \text{-------}\rightarrow \quad OH^* \quad + \quad OH$$

Degree of degradation by addition of H_2O_2 increases with the greater attribution of OH* radical, as OH* radical formed degrade the dye chromophore efficiently.[9,10]

However, some drawbacks have also been found with its use as it fails to oxidize some organic pollutants. It has been investigated by that removal efficiency for Methylene Blue dye was found to be 86% with this reagent.[11] Hydrogen peroxide reagent is also found to be effective for the removal of Rhodamine –B dye with 99% efficiency as reported.[12]

2.3 Using Fenton's Reagent

The mixture of hydrogen peroxide and ferrous ion (Fe^{+2}) is known as Fenton's reagent. Use of Fenton's reagent is one of the advanced oxidation process that has been examined for the removal of various dyes. This method involves oxidation of organic pollutants, following oxidatively degradation by hydroxyl radical that is generated from H_2O_2 in presence of Fe^{+2} as a catalyst.[13,14,15]

$$Fe^{2+} \quad + \quad H_2O_2 \text{---------}\rightarrow \quad OH^* \quad + \quad OH^-$$

A rapid reaction occurs between ferrous ion and H_2O_2 with the generation of radical hydroxyl.[13-15] The efficiency of this process depends upon concentration of H_2O_2 and Fe^{2+} ions and on pH factor. As reported by some researchers, pH should be in between 3-5.[13-15] The oxidation method using Fenton's reagent completely degrade the contaminants and break down them into harmless compounds like CO_2, H_2O and inorganic salts.[16] Moreover, this method is easy to carry out, completely reacts with organic compounds, is low cost treatment and do not produce any toxic compounds during the reaction. But, still then its applications has been found to be limited as generation of ferric hydroxide sludge in excess amount remains a disposal problem.[17] This advanced oxidation method was found to be quite effective in case of Malachite Green dye with 99% removal efficiency as reported in the study.[18] For the removal of Crystal violet dye removal efficiency has been found to be 98.2% with Fenton's reagent as reported in the literature.[19]

2.4 Ozonisation Process

Ozone, known as the most powerful oxidant than other oxidising agents like Cl_2, H_2O_2. Ozone is found to be quite capable in oxidising chlorinated hydrocarbons, phenols and some other hydro carbons. The reaction mechanism involves two steps. Step 1 involves reaction occurring at pH value of 5-6, where ozone is present as in form of O_3 and undergoes reaction with double bond of dye molecules selectively. Step 2 involves reaction taking place at higher pH value i.e. above 8 pH, where ozone readily undergoes decomposition generating hydroxyl radicals that reacts non-selectively with organic compounds.[20]

Ozonization has been found successful in removing dyes from textile effluents.[21,22] According to some researchers, reactive class of dyes show high extent of degradation with O_3 while, results found are moderate in case of basic dyes and poor results in case of disperse dyes.[23] The major advantage of this method is the application of ozone in its gaseous state and there is no sludge generation which makes it a effective tool of decolourization but, its high cost and short half-life are the barriers associated with ozonization process.[20,24] Nearly about 98% removal efficiency has been found for Rhodamine-B dye with ozonization method.[25]

2.5 Electro-Coagulation Process

A simple, reliable electro-coagulation technique has been found to be effective tool in the removal of dyes with promising better results. The method involves 3 stages.

Stage 1 involves generation of coagulants after oxidation of sacrificial anodic electrodes.

Stage 2 involves destabilization of pollutants and emulsions break out.

Stage 3 involves formation of flocs.

Figure 2 shows the diagrammatic representation of different stages of electro-coagulation process stage wise.

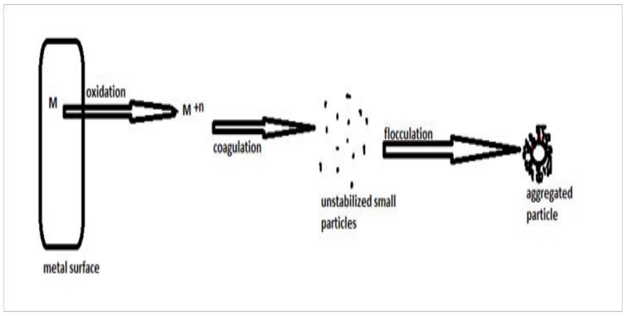

Figure 2. The diagrammatic representation of different stages of electro-coagulation process stage wise.

This method involves coagulants formation within the reactor site without the help of any external agency. Formation of coagulants is followed by oxidation of sacrificial anodic electrodes like Aluminium, Iron, stainless steel and many others, which further results in formation of hydroxyl species that helps to neutralize electrostatic charge of solids and enhancing the rate of agglomeration. The process is found to be quite effective in the removal of contaminants, colloidal particles, metal ions and dyes.[26]

Mechanism involving Aluminium electrode-

Upon oxidation, Al tends to produce aluminium hydroxide ions which further polymerises to form $Al(OH)_{3n}$ species.[26]

Step 1- $Al(s) \longrightarrow Al^{3+}(aq)$

Step 2- $Al^{3+}(aq) + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$

Step 3- $n\,Al(OH)_3 \longrightarrow Al(OH)_{3n}$

2.5.1 Mechanism involving Iron Electrode

The dissolution of iron electrode undergoes to produce ferrous-hydroxide ions $Fe(OH)_2$ in an electrolyte solution.[26]

$Fe \longrightarrow Fe^{+2}(aq) + 2e^-$ anodic reaction

$Fe^{+2}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2(s)$

cathodic reaction

$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$

Overall reaction-

$Fe(s) + 2H_20(l) \longrightarrow Fe(OH)_2(s) + H_2(aq)$

The ferrous hydroxide formed acts as a coagulant that binds the organic pollutants by electrostatic attractions and removes them through coagulation phenomena.[27]

For the removal of Methylene Blue dye, iron electrodes were found to be more efficient with 100% removal efficiency[28] and 96% removal efficiency with Fe-Al electrodes.[28] About 80% removal efficiency for Methylene blue dye has been notified with use of Fe electrode alone.[29] For the removal of Malachite Green dye, stainless steel as an electrode was found to be more effective with 99.5% removal efficiency.[30] Al electrodes have been also tried for the removal of Malachite green & Crystal violet dyes with 85% and 99.75% efficiency respectively.[31,32]

2.5.2 Electrocoagulation in Combination with Adsorption

In order to retard the generation of toxic chlorinated organic byproducts during the treatment process of dyes, it has been preferred to follow electro coagulation-adsorption technique, which is found to be more safe and efficient for the removal of dyes. Moreover, it avoids the periodical replacement of sacrificial anodes which otherwise would be costly affair.[33] A widely used adsorption technique is basically the accumulation of organic pollutant called adsorbate onto the surface of adsorbing phase called adsorbent.[34] For achieving better results for the removal of cationic and anionic dyes, a electro coagulation technique in combination with adsorption process has been carried out. Fe electrodes in combination with activated carbon and sludge derived carbonaceous material have been examined for Malachite green dye with 99.2% and 99.1% efficiency respectively.[35] For the removal of Methylene dye Al and stainless steel have been used as electrodes in combination with Banana peels to carry out dye extraction process with 99% removal efficiency.[36] Not only better dye removal efficiency but it is also found to be helpful in reducing sewage sludge pollution. Table 2 represents the removal efficiency of dyes with different electrodes through electro-coagulation process.

Table 2. Represents the removal efficiency of dyes with different electrodes through electro-coagulation process

Name of dye	Elect-rodes	Adsorbent	Removal %age	Refe-rence
Methylene Blue	Fe	----	100%	In[28]
	Al and stainless steel	Banana peel in couple	99%	In[36]
	Fe-Al	-------	96%	In[28]
	Fe		80%	In[29]
Malachite Green	Stainless steel	-----	99.5%	In[30]
	Fe	Commercial activated	99.2%	In[35]
	Fe	Carbon Carbonaceous material	99.1%	In[35]
	Al	-----	85%	In[31]
Crystal violet	Al	------	99.75%	In[32]

2.6 Solvent-Extraction Method

A newly investigated technique solvent extraction either solid-liquid or liquid-liquid extraction has been introduced with maximum extraction efficiency for the extraction of dyes from textile effluents. Solvent extraction is significant potential for the dye removal from textile waste water. The basic principle involves distribution of solute in certain ratio in b/w two immiscible solvents or we can say that mixing of known amount of dye phase in an aqueous phase and solvent phases. This method has been tried out for the removal of Methylene Blue dye using liquid-liquid extraction technique.[37] For the extraction process, benzoic acid as diluent phase has been taken with xylene and toluene as extractants in 1:1 extraction phase ratio providing the extraction efficiency of 99% and 95% respectively.[37] For the removal of Crystal violet dye, Tributyl phosphate as extractant with diluents 1-Dodecanol in 1:1 extraction phase ratio has been tried out.[38] About 90% extraction efficiency has been found for Crystal violet dye with this method.[38] Solvent extraction method has been also investigated for the extraction of Malachite Green dye and it has been found 98.67% extraction of dye with this.[39] To carry out the solvent extraction process xylene, chloroform, benzene, toluene and hexane were taken as diluents for o-chlorobenzoic acid (as extractant). But, xylene has been selected more efficient diluent for o-chlorobenzoic acid because it is little less harmful than others while almost equal removal efficiency has been reported with all of them. For the extraction of Malachite green dye. Solvent extraction process has also been carried out with 2-nitro benzoic acid as diluent for benzene (as extractant) and it has been observed 98.95% dye extraction at pH 7.[40] In the dye extraction process. Being Rhodamine-B a cationic dye, it has found that for its extraction it requires some kind of anionic carriers (as extractant). So, phenol that acts as phenoxide anionic carrier has been tested out as an extractant for the removal of Rhodamine-B dye. For the diluent phase, xylene has been tried out among all hydrocarbons because of its less toxicity than all others. Hence, with this liquid –liquid extraction 97% dye extraction has been reported.[41] Some other researcher tried out corn oil and soyabean oil as diluents for tributyl phosphate (as extractant) with 96% and 95.4% extraction efficiency respectively.[42] Therefore, selection of diluents and extractant determines the removal efficiency of dye and of extraction process which in turn also depends on its mass of transfer rate.[43]

Ease of operating and high purity is some of the advantageous associated with this technique that makes it another effective method of treatment.[44] This process has been found more advantageous as solvent recovery and dye recovery is possible in this dye extraction process.

2.7 Use of Surfactants in Solvent Extraction

Removal of dyes has also been reported by using solvent extraction method using surfactants. Encapsulation of dye in Reverse micelle from aqueous phase with the separation of solvent phase results in separation of dye from water. The extraction of different ionic dyes such as Methylene blue, Malachite green, Rhodamine-B, Crystal violet and Safranin-O dyes from aqueous phase in the presence of different surfactants-cationic or anionic has been discussed in this present study. Reverse micelle have also achieved successful results in the protein extraction and in enzyme extraction by liquid-liquid extraction process.[45-48] Removal of dyes using reverse micelle allows the solvent and dye recovery using counterionic surfactants through back extraction process.[49] Anionic surfactants like Sodium Dodecylbenzene Sulfonate (SDBS) and Sodium bis (2- ethyl) Sulfosuccinate (AOT) have been reported for the extraction of Methylene blue and Malachite green dyes.[49] For Methylene blue dye, 98% and 97% extraction efficiency has been reported with 45mg SDBS/ 50ml amyl alcohol and 45mg AOT/ 50 ml amyl alcohol respectively. For Malachite green dye 59% and 65% extraction efficiency has been studied with AOT/ isooctane and AOT/ methyl benzoate respectively. Rate of separation has been observed faster when amyl alcohol(polar medium) has been used as a solvent in comparison with benzyl alcohol and methyl-benzoate. Formation of interface at the bottom with the amyl alcohol as a solvent is lighter than water so moves upward, doing faster separation. This is because lighter solvent phase (with amyl alcohol) moves upward while heavier solvent phase (with benzyl alcohol and methyl benzoate) moves downwards. Hence, lowering the rate of separation.[49]

Table 3 shows the dye extraction efficiency with solvent extraction method either solid-liquid extraction or liquid-liquid extraction.

3. Physical Methods for the Removal of Dyes

3.1 Adsorption

Another most popular practice in the dye removal is Adsorption technique. This physico-chemical technique has been found to be most simple and economical for the removal of dyes from textile effluents.[50] A number of low cost materials including agricultural waste material, naturally found material and industrial waste material have been tried out for the removal of dyes. Even though, the adsorption capacity with these adsorbents were not found much large but still they are widely needed as they are found to be cost effective, eco-friendly and somewhat effective.[51] Various types of materials have been used as adsorbents. Some of them are reported here.

3.1.1 Industrial Waste Material as Adsorbent for

Table 3. Shows the dye extraction efficiency with solvent extraction method either solid-liquid extraction or liquid-liquid extraction

Name of dye	Diluents	extractant	%removal efficiency	Reference
Methylene Blue	Benzoic acid	Xylene	99%	In[37]
		Toluene	95%	In[37]
	SDBS	amyl alcohol	98%	In[49]
	AOT	amyl alcohol	97%	In[49]
Crystal Violet	Tributyl phosphate	1-Dodecanol	90%	In[38]
Malachite Green	Xylene Chloroform Benzene Toluene Hexane	Ortho chloro benzoic acid	98.67% 99.02% 98.33% 0% 0%	In[39]
	AOT	Isooctane	59%	In[49]
	AOT	methyl benzoate	65%	In[49]
	2-nitro benzoic acid	Benzene	98.95%	In[40]
Rhodamine-B	Corn oil soyabean oil	Tributyl phosphate	96% 95.4%	In[42]
	Xylene	Phenol	97%	In[41]

Dye Removal

Industrial waste materials such as metal hydroxide sludge, fly ash, red mud, activated carbon, coal ash have been examined as low cost adsorbents to carry out decolorization process.

3.1.2 Using Activated Carbon

Activated carbon is one of the commonly adopted adsorbent material for the removal of organic pollutants from textile effluents.[52,53] Dyes which are less soluble in water shows slow rate of adsorption on carbon content while, water soluble dyes like acidic-basic dyes and reactive dyes do not get readily adsorbed on carbon. The reason behind their poor adsorption is the polar nature of these dyes vs. non polar nature of carbon. Hence, adsorption on carbon would be less efficient when used alone. But, it becomes more efficient adsorbent when used along with coagulants. Although, Activated carbon has been found to be quite effective in removal of dyes but due to its high cost and loss of adsorbent during the deactivation, forces the researchers in seek of replacing it with some low cost adsorbents.[53]

For the extraction of Malachite Green dye 49% removal efficiency has been reported.[54] Activated carbon prepared from Durian seeds shows 48% removal efficiency for this dye and about 29% removal efficiency for Methylene Blue dye.[55,56] Coal based activated carbon shows 33% adsorption efficiency for Malachite Green dye as reported in the study.[57] Nearly about 15% removal efficiency was noticed with activated carbon prepared from oil palm fibres.[58] Activated carbon obtained from dead leaflets of Date Palm tree has been selected as renewable natural adsorbent material for the removal of Crystal violet dye with 4% removal efficiency.[59]

3.1.3 Using Sludge

Metal hydroxide sludge is one of the industrial waste materials that have been used as adsorbent for the separation of dyes from textile effluents. Hydroxide sludge contains hydroxide ions of metal and its salts.[60] For the Rhodamine-B dye, metal hydroxide sludge was found to have 4.2% adsorption as reported in the literature study.[61]

3.1.4 Using Red Mud

Red mud is other industrial waste material that has been tried out as adsorbent. Red mud has been discharged as bauxite processing residue during Alumina production.[62] Nearly about 34% removal efficiency has been reported with red mud for Malachite Green dye.[63] It has been also investigated as most effective adsorbent for the removal of Safranin-O dye with 93.2% removal efficiency using Red mud.[64]

3.1.5 Fly Ash

Fly ash is one of the industrial by-product that has been used for the removal of dyes. Baggase fly ash is one of the by-product of sugar industry which is cheaply available in plenty. It has been examined as suitable adsorbent as fly ash of sugarcane baggase does not contain any toxic metal. Baggase fly ash has been tried out as adsorbent for the removal of Malachite Green dye form aqueous solution with 17% adsorption.[65] For the Safranin-O dye very less removal efficiency was observed with this i.e. 0.2% removal efficiency.[66] NaOH modified flyash has also been examined with 93% removal efficiency for the Crystal violet dye.[67]

4. Naturally Occurring Adsorbents for Dye Removal

4.1 Using Clay

Clay is one of the naturally available adsorbent that has been extensively used for the dye removal. It has been found to be effective adsorbent because of its layered structure that works as host material for adsorbents and its counter ions. Clay particles possess strong affinity towards cations and anions as its surface area have exchangeable ions that play an important role in adsorption phenomena.[68]

Low cost powder form of Kaolin Clay has been used as adsorbent for the removal of Malachite Green, Rhodamine-B and Safranin-O dyes with 7%, 5% and 2% respectively.[69-71] Bentonite Clay has been tried out for the removal of Rhodamine-B with maximum adsorption of 83%, Methylene Blue with 99.9% removal efficiency.[72] Malachite Green dye with 18% removal efficiency with the clay as adsorbent material.[73] One other class of Clay i.e. Algerian Clay has also been examined for the removal of Methylene Blue dye with 6% adsorption.[74] Local category of clay has also been examined with 82% removal efficiency for the removal of Crytal violet dye.[75]

4.2 Surfactant Modified Clay

In order to enhance the adsorption capacity naturally available Montmorillonite Clay was made surfactant modified Clay thereby amended with Hexadecyltrimethyl ammonium bromide (HDTMA) and hexadecylpyridinium chloride (HDPy)- a cationic surfactants and with the application of surfactant modified clay 28% and 30% removal efficiency has been noticed for *Methylene blue* and Malachite green dyes.[76]

4.3 Surfactant Modified Alumina

Alumina surface was modified with the use of sodium dodecyl sulphate for waste water treatment. This surfactant modified alumina was tried out as a adsorbent for the removal of Malachite Green dye with 99% efficiency.[77] The removal efficiency of alumina modified with sodium dodecyl sulphate- an anionic surfactant has also been examined with 99% extraction for Crystal violet dye.[78]

4.4 Peat

Peat, one of the porous adsorbent materials found naturally has been tried out for the removal of various organic pollutants and dyes. It has been investigated as an adsorbent for the removal of Rhodamine-B from industrial effluents but only 8.6% removal efficiency has been reported.[79]

5. Agricultural Waste Material as Adsorbent for Dye Removal

Agricultural waste materials are cheap and easily available adsorbents that have greater potential for the removal of dyes. The utilization of these agricultural residues play a significant role in decolourization process and in national economy.[80] Some of these agricultural adsorbents have been discussed as such.

5.1 Using *Casuarina equisetifolia* Needle (CEN)

Casuarina equisetifolia needle also known as Australian pine tree is a non-leguminous plant. It can be easily processed into powder form for the process of adsorption because of its brittleness.[81] Moreover, it contain lignocellulosic material that play its role for the adsorption of pollutant material. Hence, it has been chosen for the removal of organic pollutants. *Casuarina equisetifolia* needle has been used as a adsorbent for the removal of Rhodamine-B dye with 8.2% dye removal efficiency.[82]

5.2 Durian Seeds

Durian fruit belongs to Bombacaceae family, one of the popular seasonal fruit. Inedible part of fruit that includes seeds and outer skin usually discarded as waste material. This discarded material possesses a unique characteristic of adsorbent. It has been tried out as an adsorbent for the removal of Malachite Green dye with removal efficiency of 48%.[55]

5.3 *Annona squamosa* Seeds

Annona squamosa seeds were of hedge plant, which bears delicious fruit full of nutrition and non-edible seed part were used to discard. Later on, it was investigated as an adsorbent material for the removal of Malachite Green and *Methylene Blue dye*. About 26% adsorption was observed for Malachite Green dye but very less adsorption i.e. 9% for the Methylene Blue dye has been notified.[83]

5.4 Bread Nut

One of the other low cost adsorbent bread nuts has been investigated for the removal of Malachite Green dye. Bread nut is basically an Artocorpus fruit. The seeds of this fruit were edible part while core and skin cover were non-edible which, were discarded as waste. This discarded waste fruit peels possess property of adsorption towards Malachite Green dye. Hence, nearly about 35% removal efficiency has been notified with NaOH treated bread nut.[84]

5.5 Rice Straw

Rice straw is agricultural residue used as an adsorbent material. It consists of cellulose (37.4%), hemicellulose (45%), lignin (5%) and silica ash (13.1%). For the removal of Malachite Green dye, rice straw has been used as a adsorbing material and found that unmodified rice straw shows less adsorption i.e. 9% while, rice straw on treating with citric acid shows more adsorption i.e. 26% for Malachite Green dye.[85]

5.6 Cucumis sativus

One of the home garden vegetable, *Cucumis sativus* has also been tested as adsorbent for the removal of Rhodamine –B and Crystal violet dye. It has been examined 34% adsorption for Rhodamine-B dye and 3.3% adsorption for Crystal violet dye with the use of *Cucumis sativus*, agricultural waste material.[86]

6. Biological Treatment Process

The biological method is applicable in order to remove dissolved organic matter from textile effluents. The removal efficiency depends upon the ratio of organic load vs. dye load and micro-organism load, temperature range as well as on the concentration of O_2.[87]

Bio-decolorization process carried out by variety of micro-organisms such as algae, fungi and bacteria. These bio-sorbents found to be low cost, available as dead or living micro-organism, from the breeding of mushrooms, peat, chitosan and plant waste.[88,89]

6.1 Bacteria

For the removal of Methylene blue dye various bacterial sp. such as *Pseudomonas putida, Pseudomonas aeruginosa, Aeromonas hydrophila, P. plecoglossicida, Lysinibacillus fusiformis, P. monteilli, Comamonas testosterone* and *Corynebacterium glutamicum* with removal efficiency of 69%, 82%, 40%, 34%, 25%, 47%, 40% and 39% respectively.[90-92] Bacterial sp. such as *Kurthia, Pseudomonas putida, Aeromonas hydrophila, P.plecoglossicida, Lysinibacillus fusiformis, P. monteilli, Comamonas testosterone* have also been tried for the removal of Malachite green dye with removal efficiency of 96%, 91%, 87%, 50%, 77%, 18% and 14% respectively.[90,93] For the Rhodamine-B dye bacteria like *Pseudomonas putida, Aeromonas hydrophila*, *P. plecoglossicida, Lysinibacillus fusiformis, P. monteilli* and *Comamonas testosterone* have been used for the extraction efficiency of 55%, 50%, 55%, 46%, 56% and 56% respectively.[90] Research has been also carried out for the removal of Crystal violet dye with the use of *Pseudomonas putida, Aeromonas hydrophila, Micrococcus lylae, Bacillus pumilus, Pseudomonas aeruginosa* and *Proteus vulgaris* with the extraction efficiency of 80%, 91%, 89%, 87%, 85% and 94% respectively. For the extraction of Safranin-O dye *Aeromonas hydrophila* has been tested with 70% extraction efficiency.[94-98].

6.2 Fungi

Biodesorption of Methylene blue has also been carried out with *Aspergillus fumigates*, dead fungal sp. with 80% removal efficiency.[99] Some other fungal sp. such as *Ischnoderma resinosum, Fusarium solani Aspergillus flavus and Alternaria solani* for Malachite green dye with the extraction efficiency of 97%, 96%, >96%, >96% respectively. Marine derived *Pencillium janthinellum P1* fungi sp. has been studied broadly for the bio-adsorption of Crystal violet dye and 57% removal efficiency has been noticed with this.[100-103] The fungi *Fusarium solani* and *Ischnoderma resinosum* has also been tested as bio-sorbent for the Crystal violet dye with 96% and 96.6% removal efficiency respectively.[100,101] Biosorbent prepared from wood rotting dead macro-fungus *Fomitopsis carnea,* one of the fungal specie shows 76% removal efficiency for the Safranin-O dye.[104] Fungi sp. *Penicillium expansm* and *Aspergillus niger* isolated from fruits and vegetables have been studied for the extraction of Safranin-O dye. The result found to be 41% with *P. expansm* and 39% with *Aspergillus niger sp.* at about 120 hrs reaction time.[105] For

Table 4. Represents the removal efficiency of some target dyes with the use of different species of bacteria, algae and fungi

Dye	Type	species	Removal efficiency	Reference
Methylene Blue	bacteria	*Pseudomonas putida*	69%	In[90]
		Pseudomonas aeruginosa	82%	In[90]
		Aeromonas hydrophila	40%	In[90]
		P. plecoglossicida	34%	In[90]
		Lysinibacillus fusiformis	25%	In[90]
		P.monteilli	47%	In[90]
		Comamonas testosteroni	40%	In[90]
		Corynebacterium glutamicum	39%	In[92]
	fungi	*Aspergillus fumigates*	80%	In[99]

Malachite Green	bacteria	*Kurthia sp.*	96%	In[93]
		Pseudomonas putida	91%	In[90]
		Aeromonas hydrophila	87%	In[90]
		P.plecoglossicida	50%	In[90]
		Lysinibacillus fusiformis	77%	In[90]
Malachite green		*P.monteilli*	18%	In[90]
		Comamonas testosterone	14%	In[90]
	fungi	*Ischnodermaresinosum*	97%	In [100]
		Fusarium solani	96%	In [101]
		Aspergillus flavus	>96%	In [102]
		Alternaria solani	>96%	In [102]
	Algae	*Chlorella sp.*	92%	In [106]
		Cosmorium sp.	91%	In [106]
		Euglena sp.	87%	In [106]
Rhodamine-B	Bacteria	*Pseudomonas putida*	55%	In [90]
		Aeromonas hydrophila	50%	In [90]
		P.plecoglossicida	55%	In [90]
		Lysinibacillus fusiformis	46%	In [90]
		P.monteilli	56%	In [90]
		Comamonas testosterone	56%	In [90]
	fungi	*Rhizopus oryzae*	90%	In [103]
Crystal Violet	bacteria	*Pseudomonas putida*	80%	In [94]
		Aeromonas hydrophila	91%	In [95]
		Micrococcus lylae	89%	In [96]
		Bacillus pumilus	87%	In [96]
		Pseudomonas aeruginosa	85%	In [97]
		Proteus vulgaris	94%	In [97]
	Fungi	*Penicillium janthinellum P1*	57%	In [103]
		Fusarium solani	96%	In [101]
		Ischnoderma resinosum	99.6%	In [100]
Safranin-O	bacteria	*Aeromonas hydrophila*	70%	In [98]
	Fungi	*Fomitopsis carriea*	76%	In [104]
		Fomitopsis carnea	76%	In [104]
		Penicillium expansm	41%	In [105]
		Aspergillus niger	39%	In [105]

the removal of Rhodamine-B dye, research has been carried out with fungi *Rhizopus oryzae* and was found to show 90% efficiency.[103]

6.3 Algae

One of the class of micro-organism, Algae has also been tried out as biosorbent for the removal of the dye. Some algae species have been tested to carry out bio-decolourization treatment of dyes.[106] *Chlorella sp., Cosmorium* sp. and *Euglena* sp. have been tested as bio-sorbents for the removal of Malachite green dye and found to have 92%, 91% and 87% removal efficiency respectively.[106] Table 4 represents the removal efficiency of some target dyes with the use of different species of bacteria, algae and fungi.

7. Comparative Study of Removal of Dyes using Various Methods

7.1 Removal of Rhodamine B Dye

The Rhodamine B dye is synthetic class of dye that has been widely used as a colouring agent in the textile and food manufacturing industry.[107] Exposure to this dye leads to many health effects like subcutaneous tissue borne sarcoma which is carcinogenic.[108] Many other kinds of toxicity have also been medically proven like reproductive and neurotoxicity.[108] The no. of adsorbents that have been tried out for its removal has been illustrated in Table 5. Dye removal efficiency for Rhodamine –B dye has been found to be maximums with chemical method involving advanced oxidation process and solvent extraction method. Removal efficiency of 98% was found with ozonizationtechnique and with hydrogen peroxide reagent.[12,25] More than 95% dye removal efficiency has been observed with liquid/liquid extraction involving xylene with phenol, tributyl phosphate with corn oil and soyabean oil.[41,42] Removal efficiency with biological method was found to be maximums with *P. monteilii* and *Comamonas testosterone* bacterial species i.e. 56%.[90] Other bacterial species named as *Pseudomonas putida* and *P.plecoglossicida* shows 55% removal efficiency for the removal of Rhodamine-B dye while 50% removal efficiency was observed for *Aeromonas hydrophilla* sp one of other biosorbent Pencillium was found to possess 11% removal efficiency when treated with cetlpridinium chloride and 9% removal efficiency with untreated pencillium.[109] Nearly about 34% dye removal efficiency has been examined with *Cucumis sativus* one of the agricultural adsorbent.[86] Among natural adsorbents Bentonite clay was found to be more efficient with 83% removal efficiency whereas, only 5% adsorption was observed with Kaolinite clay.[70,72] Other natural adsorbent Peat shows only 8.6% adsorption for this dye.[79] Among agricultural adsorbents CEN shows 8.2% adsorption and *Shorea dasyphylla* shows 2.4% adsorption.[89,110] Very less extraction of dye has been noticed in case of industrial adsorbents like 4.2% dye removal efficiency with metal hydroxide sludge and 2% dye removal efficiency with anaerobic sludge and 0.3% with coal ash and with agricultural adsorbent like coffee ground powder with 0.5% dye removal efficiency for Rhodamine-B dye.[61,111,112] Table 5 Shows the dye removal efficiency for Rhodamine-B dye with different reagents/ adsorbents/ biosorbents.

Table 5. Shows the dye removal efficiency for Rhoda mine-B dye with different reagents/ adsorbents/biosorbents

Reagent/Adsorbent	Type of process	Removal %age	Reference
H_2O_2	Advanced oxidation	99%	In [12]
UV/Ozone	Advanced oxidation	98%	In [25]
Xylene with phenol	Surfactant	97%	In [41]
Corn oil with tributyl phosphate	surfactant	96%	In [42]
Soyabean oil with tributyl phosphate	surfactant	95.4%	In [42]
Rhizopusoryzae	Fungi	90%	In [103]
Bentonite clay	Natural	83%	In [72]
Comamonas testosterone	Bacteria	56%	In [90]
P.monteilli	Bacteria	56%	In [90]
Pseudomonas putida	Bacteria	55%	In [90]
P. plecoglossicida	Bacteria	55%	In [90]
Aeromonas hydrophila	Bacteria	50%	In [90]
Lysinibacillus fusiformis	Bacteria	46%	In [90]
Cucumis sativus	agricultural	34%	In [86]
Cetlpyridinium chloride modified Pencillium	biosorbent	11%	In [109]
Pencillium	Biosorbent	9%	In [109]
Peat	natural	8.6%	In [79]
Casuarina equisetifolia needle CEN	agricultural	8.2%	In [82]
Kaolinite clay	Natural	5%	In [70]
Metal hydroxide sludge	industrial	4.2%	In [61]
Base treated *Shorea dasyphylla* sawdust	agricultural	2.44%	In [110]
Anaerobic sludge	industrial	2%	In [111]
Coffee ground powder	Agricultural	0.5%	In [111]
Coal ash	Industrial	0.3%	In [112]

7.2 Removal of Malachite Green Dye

Malachite Green dye is cationic type dye which is water soluble and appears in green crystalline powder form.[113]

It is used as a dye material in leather, silk, paper, paint and printing industry.[113] Other than industries we may also find its use to catch thieves and pilferers. This powder is usually sprinkled on money and anybody handling this money will find that upon washing the hands, it leaves green stains on the skin that longs for many days.[114] The number of adsorbents that has been tried out for its removal have been listed in the Table 5. More than 98% dye removal efficiency has been notified with chemical treatment of dye extraction involving reagents and electrodes like 99.5% extraction with the use of stainless steel as electrodes, 99.2% extraction with the use of iron electrode, 99% extraction with use of Fenton's reagent.[18,30,35] Maximum extraction of dye has also been observed with solvent extraction using surfactants such as use of orthochloro benzoic acid with chloroform, xylene, and benzene as extractants.[39] Extraction of Malachite green dye has also been carried with the use of bacteria, algae and fungi sp. with better dye extraction efficiency i.e 97% efficiency with *Ischnoderma resinosum*, 96% efficiency with *Fusarium solani*, *Aspergillus flavus*, *Alternaria solani, Kurthia sp.* 92% efficiency with *Chlorella* sp., 77% efficiency with *Lysinbacillus fusiformis* and 50% efficiency with *P. plecoglossicida*.[90,93,100,101,102,106] Activated carbon has been observed with 49% dye removal efficiency and activated carbon derived from Durian seed has been observed with 48% efficiency.[54-55] Dye removal efficiency with 33% has been observed with the use of industrial adsorbents such as red mud and coal based activated carbon and 15-17% efficiency with the use of baggase flyash and oil palm fibre activated carbon as industrial adsorbents[57,58,63,65]. A class of clay if modified with surfactants tends to show 29% removal efficiency for Malachite green dye.[76] Agricultural adsorbents have been examined with 26% dye removal efficiency with the application of *A. squmosa* and rice straw when treated with citric acid.[83,85] Dye removal efficiency ranging b/w 3-6% has been noticed with saw dust (NaOH treated) and rice husk(treated with peroxide) when used as agricultural adsorbents and with fly ash when used as industrial adsorbent in dye extraction process. Nearly about 2% dye removal efficiency has been examined for Malachite green dye when wheat bran and sugarcane baggase have been used as agricultural adsorbents, Ca $(OH)_2$ treated fly ash used as industrial adsorbent.[116,118,119,120] Least removal efficiency has been notified with waste pea shell i.e. only 1%.[121] Among agricultural waste materials Pine saw dust has been also tried as adsorbent for the removal of Malachite green dye and reported dye removal efficiency is 37%.[122] Table 6 shows the dye removal efficiency for Malachite green dye with various adsorbents/ reagents/ biosorbents.

Table 6. Shows the dye removal efficiency for Malachite green dye with various adsorbent/reagents/ bio-sorbents

Adsorbent/reagent/ biosorbents	Type	Removal %age	Reference
Stainless steel	Electro coagulation	99.5%	In [30]
Fe electrode(commercial activated)	Electro coagulation	99.2%	In [35]
Fe electrode(carbonaceous material)	electro coagulation	99.1%	In [35]
H_2O_2/Fe^{+2}	Fenton's reagent	99%	In [18]
Alumina modified with sodium dodecyl sulphate	natural	99%	In [77]
Orthochloro benzoic acid with chloroform	Surfactant	99.02%	In [39]
2-nitro benzoic acid with benzene	surfactant	98.95%	In [40]
Orthochloro benzoic acid with xylene	Surfactant	98.67%	In [39]
Orthochloro benzoic acid with benzene	surfactant	98.33%	In [39]
Ischnoderma resinosum	Fungi	97%	In [100]
Fusaruim solani	Fungi	96%	In [101]
Aspergillus flavus	Fungi	96%	In [102]
Alternaria solani	Fungi	96%	In [102]
Kurthia sp.	Bacteria	96%	In [93]
Chlorella sp.	Algae	92%	In [106]
Cosmorium sp.	Algae	91%	In [106]
Pseudomonas putida	Bacteria	91%	In [90]
Aeromonas hydrophila	Bacteria	87%	In [90]
Euglena sp.	algae	87%	In [106]
Al electrode	Electro coagulation	85%	In [31]
Lysinbacillus fusiformis	Bacteria	77%	In [90]
AOT/ methyl benzoate	Surfactant	65%	In [49]
AOT/ isooctane	surfactant	59%	In [49]
P.plecoglossicida	bacteria	50%	In [90]
Activated carbon	industrial	49%	In [54]
Durian seed activated carbon	industrial	48%	In [55]

Pine saw dust	agricultural	37%	In [122]
NaOH modified bread nut peel	natural	35%	In [84]
Red mud	Industrial	34%	In [63]
Coal based activated carbon	Industrial	33%	In [57]
HDTMA-Clay(surfactant modified)	natural	29%	In [76]
HDPy-Clay(surfactant modified)	Natural	28%	In [76]
Rice straw treated with citric acid	Agricultural	26%	In [85]
A.squmosa	Agricultural	26%	In [83]
Bentonite clay	Natural	18%	In [73]
P.monteilli	bacteria	18%	In [96]
Bagasse fly ash	industrial	17%	In [65]
Oil palm fibre activated carbon	Industrial	15%	In [58]
Comamonas testosterone	bacteria	14%	In [90]
Unmodified rice straw	agricultural	9%	In [85]
Kaolin clay	Natural	7%	In [69]
NaOH treated saw dust	Agricultural	6%	In [115]
Flyash	Industrial	4%	In [117]
Peroxide treated rice husk	Agricultural	3%	In [116]
Wheat bran	Agricultural	2.4%	In [118]
Sugarcane baggase	Agricultural	2.3%	In [119]
$Ca(OH)_2$ treated flyash	Industrial	2%	In [120]
Waste pea shell	Natural	1%	In [121]

7.3 Removal of Crystal Violet Dye

Crystal violet dye is also known as Methyl violet 10B dye. It is triaryl methane dye, having anti-bacterial, anti-fungal and anthelmintic properties.[123] The dye has been used in paper dyeing industry and also as a component of blue-black inks for printing. But, it has also been reported as recalcitrant dye molecule with long time persistence in the environment. Hence, it is reported as mitotic poison, potent carcinogenic and clastogene that promotes growth of tumor.[123] Hence, number of adsorbents/ reagents/ biosorbents have been tested for its removal. Dye removal efficiency has been found to be maximum i.e more than 90% with electro-coagulation process using Al electrodes with Fenton's reagent, with surfactant modified alumina, and with NaOH modified flyash.[19,32,67,78] Among the bio sorbents more dye removal efficiency has been noticed with fungal sp. than bacterial sp. such as 99.6% with *Ischnoderma resinosum*, 96% with *Fusarium solani* 94% with *Proteus vulgaris* fungal sp. whereas 91% with *Aeromonas hydrophila*, 89% with *Micrococcus lylae* and 80% with *Pseudomonas putida*.[94-97,100,101] Tendu leaf one of the agricultural adsorbent has been found with 7% extraction efficiency for Crystal violet dye.[124] Least dye removal efficiency has been noticed with *Cucumis sativus*, other agricultural adsorbent.[86] Table 7 shows the dye removal efficiency with various adsorbents/ reagents/ biosorbents for Crystal Violet dye.

Table 7. Shows the removal efficiency with various adsorbents/reagents for the removal of Crystal violet dye

Adsorbent/reagent	**Type**	**%age removal**	**Refer ence**
Al electrode	Electro coagulation	99.75%	In [32]
Ischnoderma resinosum	Fungi	99.6%	In [100]
Surfactant modified alumina	natural	99%	In [79]
Fenton's reagent	Advanced oxidation	98.2%	In [19]
Fusarium solani	fungi	96%	In [101]
Proteus vulgaris	bacteria	94%	In [97]
NaOH modified flyash	Industrial	93%	In [67]
Aeromonas hydrophila	bacteria	91%	In [95]
1-Dodecanol with tributyl phosphate	Surfactant	90%	In [38]
Micrococcus lylae	Bacteria	89%	In [96]
Bacillus pumilus	Bacteria	87%	In [96]
Pseudomonas aeruginosa	bacteria	85%	In [97]
Local clay	Natural	82%	In [75]
Pseudomonas putida	Bacteria	80%	In [94]
Penicillium janthinellum P1	fungi	57%	In [103]
Tendu leaf	agricultural	7%	In [124]
Activated carbon from date palm leaflets	industrial	4%	In [59]
Cucumis sativus	Agricultural	3.3%	In [86]

7.4 Removal of Methylene Blue Dye

Methylene Blue is also known as methylthioninium chloride. Some medicinal properties have also been observed for Methylene Blue dye as it has been used to treat urinary tract infections. But, high exposure leads to many health hazards like vomiting, headache, breathing problems and other allergic reactions.[125,126] Therefore, variety of adsorbents, reagents and bio sorbents has been tried out for its removal. Some of them have been listed below in the Table 7. Highest dye removal efficiency i.e. 100% has been observed with electro-coagulation process using Fe electrodes.[28] More than 90% dye removal efficiency has been observed with bentonite clay[72] Al and stainless steel electrodes (in couple with banana peels) xylene with benzoic acid involving solvent extraction process use of amyl alcohol with SDBS/AOT in liquid-liquid extraction process and Fe-Al electrodes in electro-coagulation.[28,36,37,49] H_2O_2 reagent has been observed with 86% dye removal efficiency.[11] Among bio-sorbents *Pseudomonasaeruginosa* shows 82%, *Aspergillus fumigates* shows 80%, *Pseudomonas putida* shows 69%, 40% with *Aeromonas hydrophila and Comamonas testosterone*.[90,91,99] A class of clay if surfactant modified tends to show 29% dye removal efficiency.[76] Pomelo has been reported for extraction of this dye with 34% efficiency.[127] Agricultural adsorbent, bark powder of Teak Tree has been tried out for extraction process, showing 33% efficiency.[128] Fruit peels have also been tried out for dye extraction process but they show poor dye removal efficiency. It has been noticed that Jack fruit peels show 29% efficiency, Guava peel shows 19% efficiency, bread bean peels show 19% efficiency and pine apple stem has been found with 12% removal efficiency for Methylene Blue dye.[129-132]. One other untreated *Parthenium hystrophorous* weed has been examined with 2.4% removal efficiency for this dye.[133] Table 8 represents the removal efficiency of various adsorbents/ reagents/ biosorbents for the removal of Methylene blue dye.

Table 8. Represents the removal efficiency of various adsorbents/reagent/bio sorbents for the removal of Methylene Blue dye

Adsorbent/reagent	Type	Removal %age	Reference
Fe electrode	electro coagulation	100%	In [28]
Bentonite Clay	Natural	99.9%	In [72]
Al and stainless steel(banana peel)	Electro coagulation in couple	99%	In [36]
Xylene with benzoic acid	Surfactant	99%	In [37]
SDBS/ amyl alcohol	Surfactant	98%	In [49]
AOT/ amyl alcohol	Surfactant	97%	In [49]
Fe-Al electrode	electro coagulation	96%	In [28]
Toluene(extract ant) benzoic acid	Surfactant	95%	In [37]
H_2O_2	Oxidation	86%	In [11]
Pseudomonas aeruginosa	Bacteria	82%	In [91]
Aspergillus fumigatus	Fungi	80%	In [99]
Fe electrode	electro coagulation	80%	In [29]
Pseudomonas putida	Bacteria	69%	In [90]
P.monteilli	Bacteria	47%	In [90]
Aeromonas hydrophila	Bacteria	40%	In [90]
Comamonas testosterone	Bacteria	40%	In [90]
Cornylbacterium glutamicum	bacteria	34%	In [92]
P.plecoglossicida	Bacteria	34%	In [90]
Pomelo	Natural	34%	In [127]
Teak Tree Bark powder	Agricultural	33%	In [128]
HDTMA-Clay(surfactant modified)	Natural	30%	In [76]
HDPy-Clay(surfactant modified)	Natural	29%	In [76]
Durian shell(activated carbon)	Industrial	29%	In [56]
Jack fruit peel	Natural	29%	In [129]
Lysinibacillus fusiformis	Bacteria	25%	In [90]
Guava peel	Natural	19%	In [130]
Broad Bean peel	Natural	19%	In [131]
Pine apple stem	Natural	12%	In [132]
A.squmosa	Agricultural	9%	In [83]
Algerian clay	Natural	6%	In [74]
Parthenium hystrophorous weed(untreated)	Biosorbent	2.4%	In [133]

7.5 Removal of Safranin –O Dye

Safranin-O dye is one of the basic dye also known as basic red-2. Amorphous powder form of Safranin-O dye is highly soluble in water and form stable salts of mono-acids. Wide application of this dye was notified in textile industry but contributes to toxicity in water bodies when discharged off.[134] So variety of the adsorbents have been tried out for its removal. Some of them have been discussed below. Like one of the industrial adsorbent Red Mud was found to be effective for decolourization of this dye with 93.2% removal efficiency.[64] Among agricultural adsorbents 82% removal efficiency has been noticed with activated rice husk when tried out as a adsorbent material Biosorbents such as *Fomitopsis carnea* and *Pencillium expansum* fungal sp. shows 76% and 41% removal efficiency whereas *Aeromonas hydrophila* bacterial sp. shows 70% removal efficiency for this dye.[98,104,105,135] Seeds of mango have been also examined for the removal of Safranin-O dye. Nearly about 4.3% removal efficiency in case of treated mango seeds while 3.4% removal efficiency in case of untreated mango seeds has been notified[136]. Very less removal efficiency has been notified with natural adsorbents like only 2% adsorption with Kaolinite clay, and less than 0.4% adsorption with coffee ground and with fly ash.[66,71,137] Nearly about 4% removal efficiency has been notified with rice husk (agricultural adsorbent) when treated with NaOH.[138] Table 9 represents the removal efficiency of various adsorbents/ reagents/ biosorbents for the removal of Safranin-O dye.

Table 9. Shows the removal efficiency for Safranin-O dye with various adsorbents

adsorbent	type	Removal %age	Reference
Red mud	industrial	93.2%	In [64]
Activated rice husk	Agricultural	82%	In [135]
Fomitopsis carriea	Fungi	76%	In [104]
Fomitopsis carnea	Fungi	76%	In [104]
Aeromonas hydrophila	Bacteria	70%	In [98]
Aspergillus niger	fungi	39%	In [105]
Pencillium expansm	Fungi	41%	In [105]
Treated mango seeds	agricultural	4.3%	In [136]
NaOH treated rice husk	agricultural	4%	In [138]
Untreated mango seeds		3.4%	In [136]
Kaolinite Clay	natural	2%	In [71]
Coffee ground		0.4%	In [137]
Fly ash	industrial	0.2%	In [75]

8. Conclusion

Various methods such as adsorption, electrocoagulation, advanced oxidation method, solvent extraction and biological methods have been compared for the treatment of textile waste water. It has been concluded that removal of dyes with adsorption technique using low cost/no cost adsorbent materials like naturally occurring, agricultural and industrial waste materials, has been found to be more effective with better removal efficiency. By utilizing waste discharged residues as adsorbents thereby, would improve textile industry economically.

a) For the removal of Methylene Blue dye, Bentonite Clay one of the naturally occurring adsorbents has been found to be more effective with 99.9% removal efficiency.
b) For the removal of Safranin-O dye, Red mud one of the industrial adsorbents and activated rice husk, agricultural adsorbent, have been found to more effective with 93.2% and 82% removal efficiency respectively.
c) For the removal of Crystal Violet dye, modified alumina and NaOH treated flyash (industrial adsorbent) have been found to be more effective with 99% and 93% dye removal efficiency.
d) For the removal of Rhodamine-B dye, naturally occurring Bentonite clay as adsorbent has been found to be more efficient with 83% removal efficiency.
e) For the removal of Malachite Green dye, surfactant modified alumina (with sodium dodecyl sulphate) has been found to be more efficient with maximum removal efficiency of 99%.

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