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REMOVAL OF DYES FROM WASTEWATER BY PLANT WASTE

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ABSTRACT

Dyes are complex organic compounds which are used by various industries to colour their products.These dyes enter the water which make them polluted.Today,colour removal from wastewater has been a matter of concern, both in the aesthetic sense and health point of view. Colour removal from textile effluents on a continuous industrial scale has been given much attention in the last few years, not only because of its potential toxicity, but also mainly due to its visibility problem. There have been various promising techniques for the removal of dyes from wastewater. However, the effectiveness of adsorption for dye removal from wastewater has made it an ideal alternative to other expensive treatment methods. In this review, an extensive list of sorbent literature has been compiled. The review evaluates different agricultural waste materials as low-cost adsorbents for the removal of dyes from wastewater. The review also outlines some of the fundamental principles of dye adsorption on to adsorbents.

Keywords : Dyes Low-cost adsorbents Adsorption Wastewater treatment,Adsorption, Plant wastes, Low-cost adsorbents, Wastewater treatment.

I. INTRODUCTION

One of the major problems encountering today is the discharge of large volumes of highly coloured wastewater(dyes) in the environment which cause serious health hazards.The term which we can use for this problem is Water Pollution. Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., to colour their products. As a result, they generate a considerable amount of coloured wastewater. There are more than 10,000 commercially available dyes with over 7 × 10^5tonnes of dye stuff produced annually. It is estimated that 2 % of dyes produced annually is discharged in effluents from associated industries [1]. Among various industries, textile industry ranks first in usage of dyes for coloration of fiber. The total dye consumption of the textile industry worldwide is in excess of 107 kg/year and an estimated 90 % of this ends up on fabrics. Consequently, 1,000 tones/year or more of dyes are discharged into waste streams by the textile industry worldwide [2]. Discharge of dye-bearing wastewater into natural streams and rivers poses severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment.Dyes can be classified as natural and synthetic as explained Fig 1 :

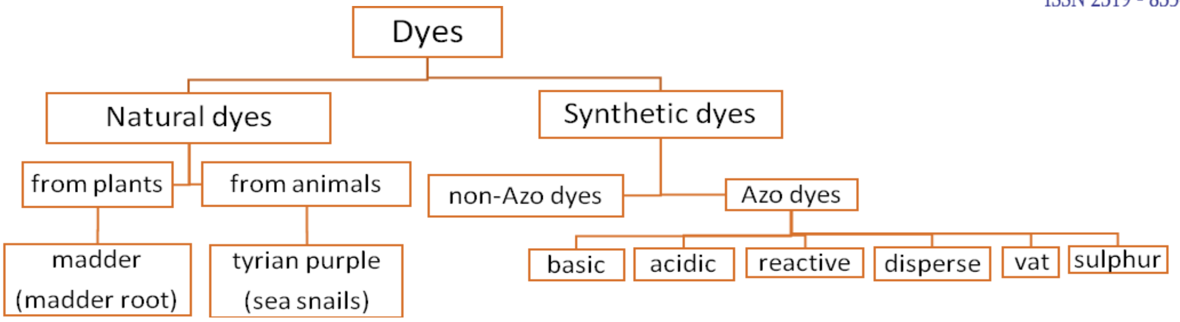


Fig 1:Classification of Dyes

II. DYES & THEIR TOXICITY EFFECTS

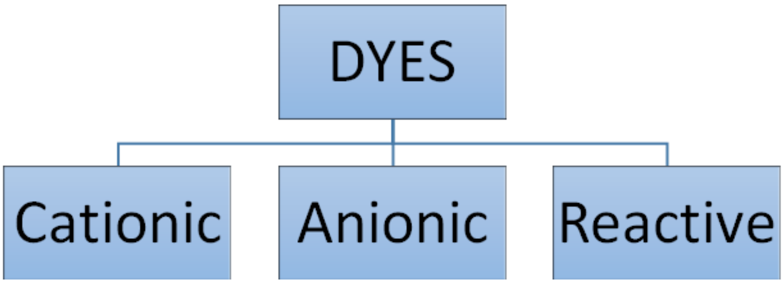


Fig 2: Types of Dyes

2.1 Cationic dyes

They are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration. Basic dyes consist of monoazoic, diazoic andazine compounds [3]. They are used to colour wool, silk, nylon, mod-acrylic and polyester materials. Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcarbenium,phthalocyanine dyes, polycarbocyclic and solvent dyes[4].Basic dye are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer [5]. Also, they can cause increased in heart rate, shock, vomiting, cyanosis, jaundice, quadriplegia, heinz body formation and tissue necrosis in humans [6].

2.2 Anionic dyes

They have negative ions due to the excess presence of the OH- ions in aqueous solution.Anionic dyes are water soluble and they include acid dyes,azo dyes, direct dyes and reactive dyes. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactivegroups in the water) that forms a covalent bond between the molecule of dye and that of the fibre[13]. Their removal is the most challenging task as they produce verybright colours in water and show acidic properties.

2.3 Reactive dyes

They contain reactive groups such as vinyl sulphone, chlorotriazine, trichloropyrimidine, and difluorochloropyrimidine that covalently bonded with the fiber during the dyeing process [7]. Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes [8]. Azo dyes have the largest varietyof dyes and under anaerobic conditions, the dye's linkage can be reduced to form aromatic amines which are colourless but can be toxic and carcinogenic [9]. It was estimated that 130 of 3,200 azo dyes in use can form carcinogenic aromatic amines during degradation process [9].

III. ADSORBATE SEPARATION METHODS

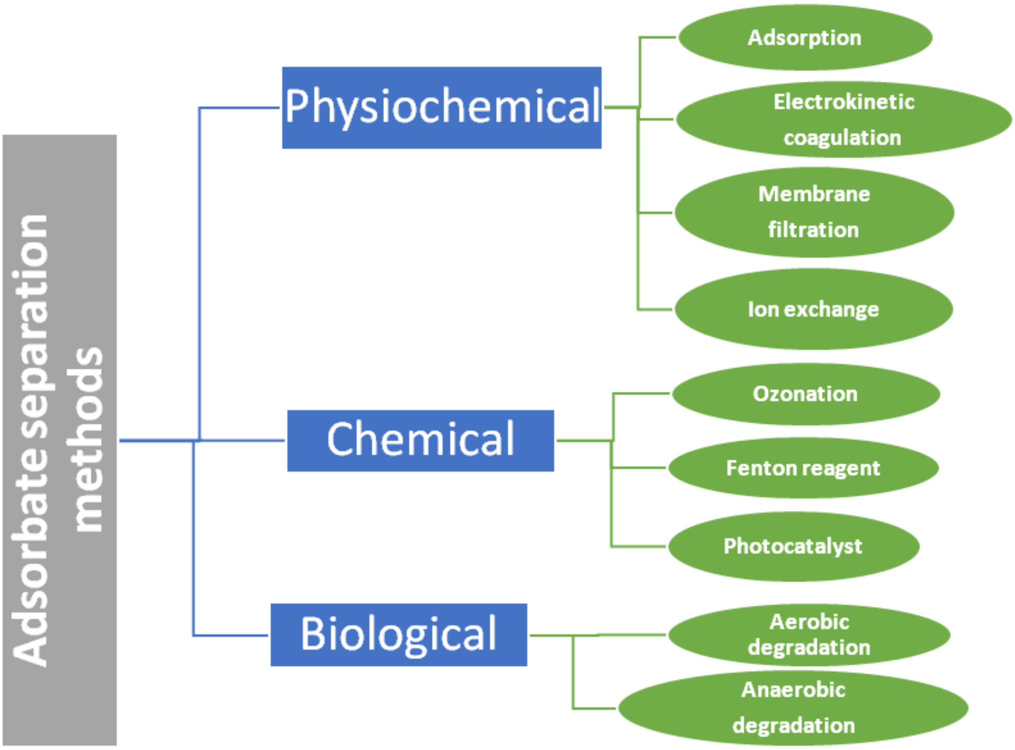


Fig 3: Adsorbate Separation Methods

3.1 Physiochemical Separation Technique

There are various types of physio-chemical methods used in the removal of dyes as part of water and waste water treatments and one of them is adsorption.

3.1.1 Adsorption

Adsorption process is a very effective separation technique and it is considered to be superior compared to other available techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances [4, 12]. The efficiency of adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate. Adsorbent's selectivity is based on the adsorption capacity, surface area, availability and total cost. Various adsorbents such as commercial activated carbon [14], mineral [15], Clay [16], agricultural solid wastes [17-19] and agricultural solid waste based activated carbon [20-22] have been used in the removal of dyesfrom wastewater.

3.1.1.1 Chemical activation of adsorbents:

Reagents such as phosphoric acid, zinc chloride, potassium hydroxide, potassium carbonate and sodium hydroxide are used in the chemical activationof carbon under different conditions [29,30]. Alkali hydroxides and zinc chloride are not preferred due to their corrosive natures and the harmful effects associated with thedisposal [39]. Potassium carbonate is used as a food addictive thus it is safe to use it as an activating agent in the production of activated carbon. AC production depends on the precursor properties, reagent used, impregnation ratio, activation time and temperature. Chemical activation has more advantages than physical activation because it is carried out in singlestep i.e. carbonization and activation are united at relatively lower temperature operation and higher yield [29,30]. Various researchers [20,22]have successfully reported the production of chemically activated biomass based AC(Activated Carbon) in the dye removal.

3.1.1.2 Physical activation of adsorbents:

Physical activation method is used to improve the porosity of AC(Activated Carbon) by exposing carbonaceous material to carbon dioxide gas, air mixture or steam under high temperature profile. An abundance of pores, particularly micropores, were generated after activation due to theoxidation of partial carbon atoms by carbon dioxide gas and steam[42]. Physical activation involves carbonization of a carbonaceous material followed by activation of the resulting charcoal at high temperature in the presence of suitableoxidizing gases where oxidization agents such as steam has shown the best potential for producing activated carbons with high surface area and good pore ratio [25]. Biomass based activated carbon (AC) through physical activation and its adsorptive behaviour has been reported by various researchers [21,33,34].

There are various cost effective adsorbent that have been successfully used in the removal of textile dyes from wastewater such as pine cone, palm-trees, papaya seeds ,rice husks etc.

Adsorbents	*Adsorbates (Dyes)*	*Adsorption capacity (mg/g)*	*References*
Coffee waste	Toluidine blue	142.5	[25]
Core pith	Congo red	2.6	[40]
Pine cone	Congo red	19.18	[19]
Date stones	Methylene blue	43.5	[28]
Palm shells	Reactive (blue/red)	14-24.7	[20]
Papaya seeds	Congo red	71	[21]
Almond shells	Direct red 80	90.09	[41]
Rice husk	Acid yellow 36	86.9	[42]
Orange peel	Aid violet	19.88	[43]
Banana peel	Basic blue	20.8	[44]
Neem bark	Malachite green	0.36	[34]
Mango bark	Malachite green	0.5	[34]
Garlic peel	Methylene blue	142.9	[44]
Sugar cane bagasse	Congo red	38	[21]
Guava leaf powder	Methylene blue	185.2	[45]
Saw dust	Methylene blue	40	[46]

Table 1 : Compilation results on various agricultural by-product adsorbent in the removal of dyes from aqueous solution.

3.1.1.3 Mechanism of adsorption

Mathematical treatment given by Reichenberg and Boyd is used to distinguish between the particle, film diffusion, and mass-action-controlled mechanisms of exchange have laid the foundations of sorption/ ion-exchange kinetics [30]. Usually, external transport is the rate-limiting step in systems, which have (a) poor mixing (b) dilute concentration of adsorbate (c) small particle size and (d) high affinity of the adsorbate for adsorbent. In contrast, the intraparticle step limits the overall transfer for those systems that have (a) high concentration of adsorbate; (b) good mixing; (c) large particle size of adsorbent; and (d) low affinity of the adsorbate for adsorbent [48]. It is now well established that during the adsorption of a solid chemical substance over a porous adsorbent following three consecutive steps taking place [21].

1. Transport of the adsorbate ions to the external surface of the adsorbent (film diffusion).
2. Transport of the adsorbate particles within the pores of adsorbent, excluding the small amount of adsorption occurring at the external surface of the adsorbent (particle diffusion).
3. Adsorption of the adsorbate ions on the interior surface.

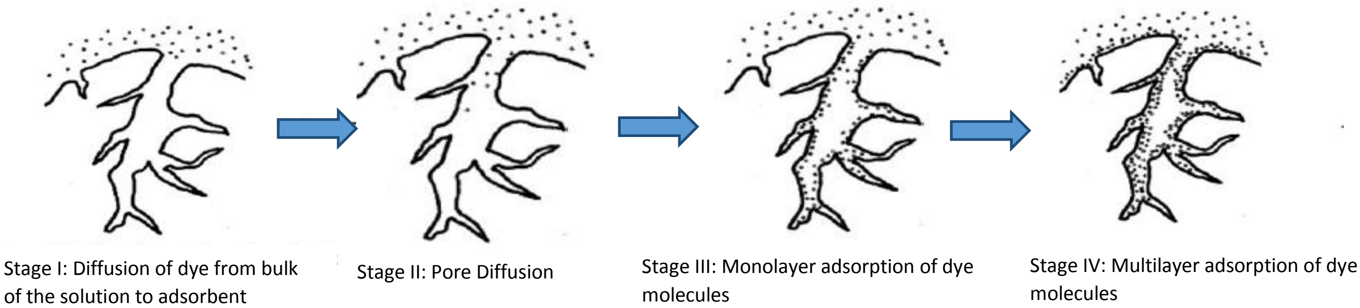


Fig 4: Steps of adsorption [21,48,30]

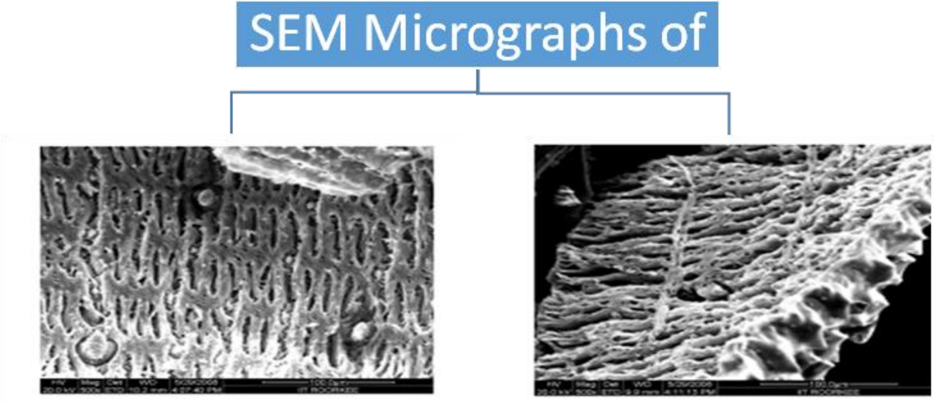
IV. PHYSICO-CHEMICAL CHARACTERIZATION OF ADSORBENTS

Proximate analysis and particle size of the RHA(Rice Husk Ash) are presented in Table 2 [48]. The SEM micrographs of $FeCl_3$coated adsorbents and Se(IV) loaded adsorbents are shown in Fig. 2. It shows surface texture and porosity of the blank and loaded adsorbents. It can be inferred from these figures that the surface texture of the blank adsorbents changes drastically after the loading of the adsorbates..

Characteristics	Value
Moisture(%)	10.07
Volatile matter(%)	15.03
Ash(%)	69.61
Fixed Carbon(%)	5.36
Average particle size(um)	410

Table 2. Proximate Analysis of RHA[4,10,48]

EDAX spectra indicates presence ofelemental selenium after adsorptiononto adsorbent as shown in Fig. 5 [48]. It indicate that at the adsorbent surface Se(IV) was reduced to elemental selenium.



(a) (Blank)RHA

(b) (Se(IV) Loaded) RHA

Fig.5(a) (Blank) RHA[4,10] and (b) (Se(IV) Loaded) RHA[4,10]

V. FACTORS AFFECTING ADSORPTION

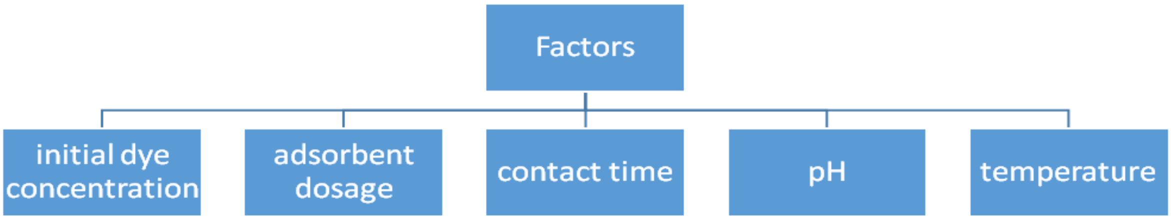


Fig 6: Factors affecting adsorption

5.1 Effect of initial dye concentration

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb afixed amount of dye . The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface [4].Normally the dye removal will decrease with increase in initial dye concentration. This is because for a given mass of adsorbent; the amount of dye it can adsorb is fixed.The higher the concentration of the dye, the smaller thevolume it can remove.[10].

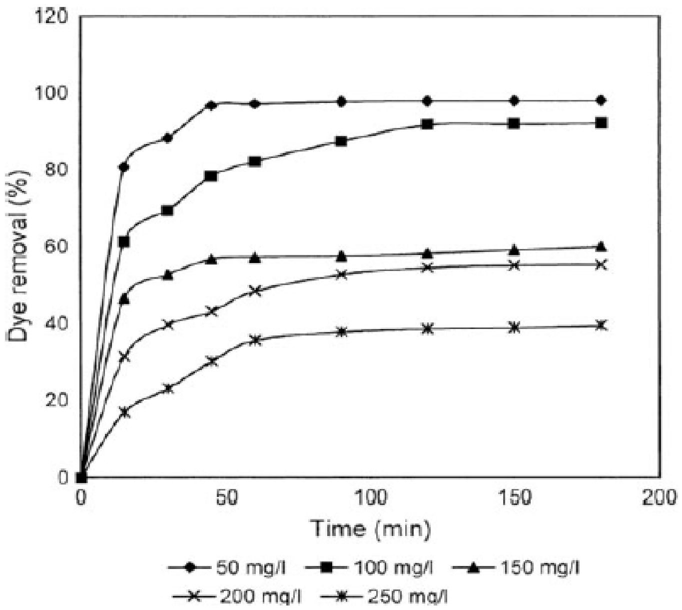


Fig 7: Adsorption of Malachite green on formaldehyde treated Prosopis cinraria sawdust [34].

5.2 Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption process can be carried out by preparing adsorbent–adsorbate solution with different amount of adsorbents added to fixed initial dye concentration and shaken together until equilibrium time [4]. Generally, the percentage of dye removal increases with increasing adsorbent dosage. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher.

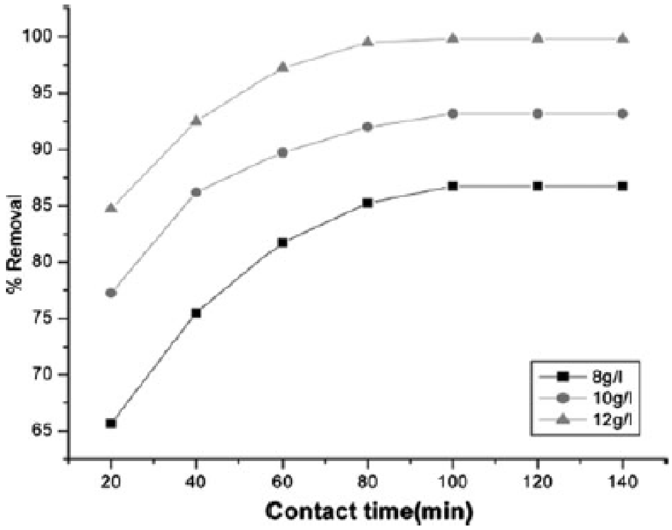


Fig 8: Effect of absorbent dose on the percent removal of methylene rice husk activated carbon [49]

5.3 Effect of contact time

The effect of contact time on adsorption of dye can becarried out by preparing adsorbent–adsorbate solution withfixed adsorbent dose and initial dye concentration for differenttime intervals and shaken until equilibrium. Generally the rate of removal of dye increases with an increase incontact time to a certain extent. Further increase in contacttime does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material[50]. At this point, theamount of the dye desorbing from the adsorbent is in a stateof dynamic equilibrium with the amount of the dye beingadsorbed onto the adsorbent.

5.4 Effect of pH

pH is a measure of acidity or basicity ofan aqueous solution. The pH factor is very important in theadsorption process especially for dye adsorption. At high pH solution, thepositive charge at the solution interface decreases and theadsorbent surface appears negatively [40]. As a result, the cationic dye adsorption increases and anionic dye adsorption shows a decrease [39].

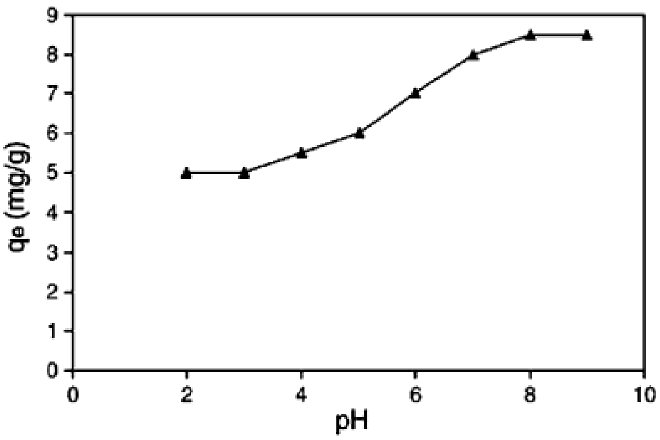


Fig 9: Effect of pH on crystal violet biosorption [40].

5.5 Effect of temperature

A study of the temperature dependence of adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption [20] Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process [39]. If the adsorption capacity increases with increasing temperature then the adsorption is an endothermic process.

VI. CONCLUSION

In this review, a wide range of agricultural waste materials, as low-cost adsorbent has been presented. The use of these low-cost bio-sorbents is recommended since they are relatively cheap or of no cost, easily available, renewable and show highly affinity for dyes. The process of bio-sorption requires further investigation in the direction of modeling, regeneration of bio-sorbent and immobilization of the waste material for enhanced efficiency and recovery. Since modification of adsorbent surface might change the properties of adsorbent, it is recommended that for any work on chemically modified plant wastes, characterization studies involving surface area, pore size, porosity, pHZPC, etc. should be carried out. Spectroscopic analyses involving Fourier transform infrared (FTIR), energy dispersive spectroscopy (EDS), X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy are also important in order to have a better understanding on the mechanism. Further more interest should be concentrated by the researchers to predict the performance of the adsorption process for dye removal from real industrial effluents.

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