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Dye Removal from Aqueous Solution using Low Cost Bioadsorbents Derived from Agricultural Waste: A Review

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Abstract: Dyes are the chemical substances which impart color upon the application to the substrate by mechanical retention, physical adsorption, covalent bond formation and complexation with salts. Different approaches for dye removal include chemical approach (electrochemical destruction, ozonation, and Fenton-like oxidation), physical approach (filtration, coagulation, adsorption and ion-exchange) and biological approach (aerobic and anaerobic oxidation, microbial cultures). However, adsorption onto low cost bioadsorbents derived from agricultural wastes in beneficial over other techniques due to sludge free procedure, recovery of adsorbent, more efficient, technically easy and non-polluting characteristics. Agricultural wastes are chemically modified using alkali, acids, oxidizing agents, surfactants; and are modified by physical activation and biological treatments to alter its pore size, physic-chemical properties, chemical composition and surface area to enhance its adsorption potential. This review focuses on various adsorbents derived from agricultural wastes as such and in its chemically modified form for the uptake of dyes from aqueous solution, different factors affecting the uptake of dyes from aqueous solution and thermodynamic parameters for the adsorption process. Mechanism for the dye removal and different adsorption isotherms applicable to its are also presented.

Keywords: Dyes, pollutant removal, toxic effects, adsorption, agricultural wastes

INTRODUCTION

Dyes are the chemical substances which upon application to the substrate imparts colour by the process that at least temporarily destroys any crystal structure of that colored substance. They are held on compatible surfaces by mechanical retention, physical adsorption, formation of covalent bond, complexes with salt solutions. Dyes are widely utilized in the textile industry, leather tanning industry, food industry, agriculture, paper industry, light harvesting arrays, photo-electrochemical cells, hair coloring and cosmetics among which textile industry is one of the major sector for the usage of synthetic dyes [1]. The approximate annual global production of dyes is about $7*10^5$ tons per year of which two-thirds is consumed by textile industry. Dyes are extensively grouped into acidic dyes, basic dyes, direct dyes, fluorescent dyes, reactive dyes, sulphurous dyes and vat dyes. Applications of various classes of dyes are summarized as follows [2]:

I.

5			
Category of dye	Dyeing Applications in textile industry		
Acidic dyes	Nylon, silk, modified acrylic, wool, paper, food and cosmetics		
Basic dyes	Modified acrylic, modified nylon, modified polyesters, papers		
Direct dyes	Cotton, regenerated cellulose, paper, leather, nylon		
Reactive dyes	Cotton, wool , nylon		
Sulphurous dyes	Cotton		
Disperse dyes	Cellulose acetate, nylon, polyester and polyamide		
Azo dyes	Polyester, nylon, cellulose diacetate, acrylic fibres		

Table 1: Dyeing applications of various categories of dyes in textile industry

The incomplete exhaustion of dyes onto textile fibre from aqueous solution is a major source of colour release into the environment and almost 1000 m³-3000 m³ is discarded after producing 12-20 tons of textile dyes per day [3]. The possible contamination of water bodies due to discharge of colored effluent produced from dyes into surrounding water bodies is resulting in environmental apprehension as dyes reduces light penetration and photosynthesis affecting aquatic living organisms; also some dyes exhibit either toxicity, mutagenicity or carcinogenicity[4,5]. Human health hazards of some dyes caused due to their unintentional or elongated period over revelation are listed below [5-8]:



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Name of dye	Hazardous effects to human beings
Methylene blue	Rise of heartbeat, vomiting, cyanosis, jaundice, quadriplegia, tissue necrosis,
	cancer, shock
Eosin yellow	Eye & skin irritation, inhibition of protein-protein interaction, triggers geno-
	toxicity in man
Methyl orange	Gene mutations, allergic dermites, cancer
Malachite green	Detrimental effects in liver, kidney, intestine and gonadotropic cells, damage of
	mitochondria, nuclear alterations

Table 2: Hazardous effects of Methylene blue, eosin yellow, methyl orange and malachite green to human beings

Different conventional techniques for dye removal can be widely grouped into physical, chemical and biological methods. Chemical approach include Fenton like reagent technique, ozonation, photo catalytic techniques and electrochemical destruction, physical approach includes adsorption, ion-exchange, filtration, coagulation and irradiation, while biological treatments include aerobic and anaerobic degradation, decolorization by white rot fungi and other microbial cultures[9,10]. The restriction in application of above mentioned methods may sometimes arise due to technical or economical feasibility. However, among above mentioned approaches adsorption is beneficial due to its possible regeneration at low cost, sludge free procedure, recovery of adsorbent, more efficient, technically easy and non polluting characteristics[11,12].



Figure 1: Different approaches for dye removal

Egyptians first utilized charcoal for adsorption of odorous vapors from wounds and intestine in 1550 BC and application of charcoal filters to purify water was studied by Phoenicians in 460 BC[11]. Adsorption is surface phenomena in which a multi-component fluid system is bounded to the surface of solid adsorbent via physical or chemical bond. There are mainly two types of adsorption: chemical adsorption (chemisorptions) or physical adsorption (physisorption). Chemical adsorption involves the formation of strong chemical bonds between adsorbate and adsorbent occurring due to exchange of electrons and the process is generally irreversible while physisorption involves the weak van der Waals intraparticle bonds between adsorbent and adsorbate or hydrogen bonds or dipole-dipole π - π interactions and hence the process mostly irreversible in most cases [10-14]. Different types of low cost adsorbents utilized for waste-water treatment can be classified as follows [10-18]:



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Name of adsorbent	Classification			
Agricultural waste	Activated carbon solid waste (Pine wood, coconut tree sawdust, rice husk,			
	orange peel)			
	Raw solid waste (Saw-dust, bark, tree-fern, husk, peel)			
Natural material	Clay and ore material(Bentonite, Kaolinite, smectite)			
	Zeolites (MCM-22) and silicous materials(SBA, MPS)			
	Soil and sediments (Montmorillonitic soil)			
Industrial waste	By-product(Fly ash, steel waste, red mud, metal hydroxide sludge, al			
	waste)			
	Activated carbon waste(Waste newspaper, Sewage sludge, blast furnace			
	slag)			
Sea materials	Chitin, chitosan, peat			
	Biomass (Yeast, seaweed, algae, fungi)			
Miscellaneous adsorbents	Starch and cyclodextrins			

Table-3: Different types of adsorbents and their classification

The mechanism of adsorption of pollutant (dyes, metal ions etc.) on adsorbate can be briefly explained by occurrence of series of following consecutive steps [11, 13, 19, 20]:



Figure-2: Different steps describing mechanism of adsorption of dye molecule onto adsorbate

The properties of dye solution affecting the removal efficiency of dye from aqueous solution are ionic strength, presence of other contaminants, pH, and initial concentration, dosage of adsorbent, temperature and agitation time. Removal efficiency of dye from aqueous solution is also influenced by adsorbent properties like specific surface area, pore volume, grain size, pore size distribution and particle size [11, 13]. Agricultural wastes are often difficult to dispose off and do not have much economic value. Biosorption based on binding capacities of agricultural wastes is imperative because of their abundant availability at no or very little cost and high-quality performance in removal of dyes with minimum amount of sludge to be disposed off [12, 21]. Various parts of plant materials or their chemically modified form employed for removal of dyes in aqueous medium include Mangifera Indica, Tephrosia Purpurea, Moringa Tinctoria, Tridox Procumbens, Azadirachta Indica, Oscimum Sanctum, Rhus Coriara L. teak leaf litter, oil tea shell, Ficus Carica, coconut shell[4,6,22,23]. This review discuss about various bioadsorbents derived from agricultural wastes for dye removal as such, or in its chemically modified form and factors affecting removal dyes from aqueous media. Different models applicable to adsorption of dyes onto bioadsorbents derived from agricultural waste, kinetic and thermodynamics of dye removal are also presented.



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A. Dye Removal Using Low Cost Bioadsorbents Derived From Agricultural Waste

The evaluation of feasibility of tea leaf litter powder for removal of eosin yellow from aqueous solution was best described by Langmuir adsorption isotherm with maximum monolayer capacity 31.64 mg/g at 303K. Kinetics of adsorption was best described by pseudo second order model at 303K and the process was influenced by boundary layer diffusion. The mechanism of uptake of eosin yellow from aqueous solution by teak leaf litter powder was governed by liquid film diffusion and intra particle diffusion; positive values of mean adsorption energy and standard enthalpy shows physisorption of dye molecules onto teak leaf litter powder [6]. Oiltea shells as such and modified with fungus Pycnoporus sp. and Trametes versicolor were evaluated for the removal Methylene blue from aqueous solution. The maximum adsorption capacity of unmodified Oiltea shells, Pycnoporus sp. and Trametes versicolor modified Oiltea shells was found to be 64.4 mg/g, 72.5 mg/g and 85.7 mg/g which indicate improved surface area and pore size as well as alteration in chemical composition and physic-chemical properties upon fungal treatment of oil tea shells. The sorption data of both Oiltea shells as such and fungus modified Oiltea shells was best represented by Langmuir adsorption isotherm and pseudo second order kinetic model; also sorption process was spontaneous and favorable[24]. Activated carbon prepared from coconut husk by sulphuric acid activation was assessed for removal of textile dyes Maxilon blue GRL and direct yellow DY 12. The kinetic studies of adsorption of Maxilon blue GRL and direct yellow DY 12 onto activated carbon prepared from coconut husk by sulphuric acid activation was best described by pseudo second order model; uptake of dye molecules from aqueous solution were best fitted to Fritz-Schlunder isotherm indicating heterogeneous and multi-layer adsorption limited by chemisorption process. The spontaneity and endothermic nature of adsorption process was evaluated by determination of Gibb's free energy, enthalpy and entropy [25]. Daucus carota (Carrot) plant waste materials stem powder and leaf powder were explored for removal of Methylene blue and malachite green from aqueous solution. The sorption of Methylene blue and a green on carrot stem and leaf powder was best described by pseudo-second order kinetic model and Langmuir and Freundlich adsorption isotherms. In earlier stages dye uptake process was influenced by surface diffusion while in later stages it was controlled by pore diffusion. Thermodynamic parameters enthalpy, entropy and Gibb's free energy indicated the adsorption process to be exothermic, spontaneous and physical in nature. The monolayer adsorption capacities of carrot leaf powder are higher than carrot stem powder and hence carrot leaf powder is better adsorbent [26]. A low cost adsorbent prepared from Annona squmosa seed by chemical activation with concentrated sulphuric was scrutinized for the removal of cationic dyes Methylene blue and malachite green from aqueous solutions. The adsorption dynamics and equilibrium data of adsorption of Methylene blue and malachite green onto adsorbent derived from Annona squmosa seed were best described by pseudo-second order model and Langmuir adsorption isotherm; the study revealed Annona squmosa seed a better adsorbent for malachite green than for Methylene blue [27]. The evaluation of potential of cauliflower leaves for the removal of Methylene blue from aqueous solution revealed that equilibrium data and adsorption kinetics were best described by Freundlich adsorption isotherm and pseudo-second order kinetic model. Feasibility, spontaneity, exothermic and physical nature of adsorption process was confirmed from the negative values of enthalpy, entropy and Gibb's free energy [28]. The equilibrium data and adsorption dynamics of adsorption of Methylene blue onto mishwak leaves was elucidated by Langmuir adsorption isotherm and pseudo second order kinetic model with maximum adsorptive capacity 200 mg/g and negative value of Gibb's free energy indicated spontaneity of adsorption process [29]. The investigation of removal of Congo red dye from aqueous solution by adsorption on charcoal derived from ground nut shells and Eichhornia showed that pseudo second order kinetic model and Freundlich adsorption isotherm best described adsorption dynamics and equilibrium data indicating heterogeneous nature of adsorption. The maximum adsorption capacity of groundnut shell derived charcoal and Eichhornia derived charcoal was found to be 117.6 and 56.8 mg/g respectively at 318K which also increased with increase in temperature [30]. The batch adsorption studies of adsorption of Methylene blue onto Punica granatum husk revealed the maximum adsorption capacity as evaluated from Sips model 68.40 mg/g; adsorption kinetics well described by pseudo second order kinetic model and adsorbent Punica granatum husk could be regenerated using 1 mol/litre HCl as eluent[31]. Biochars produced by pyrolyzing vermicompost at different temperatures were evaluated for their potential to adsorb Congo red and Methylene blue from aqueous solutions. The study led to the conclusion that increases in pyrolysis temperature of biochar synthesis increased the uptake of Congo red while reduced the uptake of Methylene blue from aqueous solution. The adsorption of Congo red and Methylene blue onto biochar follows Langmuir indicating homogenous surface having equivalent number of sites are available for adsorption of Congo red and Methylene blue and Temkin adsorption isotherm signifying chemisorption was mainly due to electrostatic interactions adsorption kinetics well fitted to pseudo second order kinetic model. The Congo red adsorption onto biochar was chiefly controlled by π - π dispersion interaction and retention of Methylene blue was mainly due to cation exchange [32]. Spent tea leaves were investigated for their ability to adsorb methyl orange from aqueous solution; response surface methodology based on Box-Behnken design was used to obtain optimum conditions initial concentration 9.75 mg/l, temperature 35.3°C, contact time 63.8 min, and



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adsorbent dosage 3.90 g/l for maximum removal 58.2 % [33]. Activated carbon derived from finger citron residue was tested for their capacity to adsorb Methylene blue and methyl orange from aqueous solutions. The results revealed that adsorption of dyes onto finger citron residue derived activated carbon was best described by Langmuir adsorption isotherm and pseudo-second order kinetic model with maximum equilibrium adsorption capacity 934.58 mg/g for Methylene blue and 581.40 mg/g for methyl orange. The high adsorptive capacity of these activated carbon compared to other bioadsorbents was due to π - π stacking interactions between the surface of activated carbon and dyes [34]. The investigation of cationic modified orange peel powder for their potential to adsorb anionic dye Congo red from aqueous solution led to the conclusion that equilibrium data and kinetics of adsorption well fitted to Langmuir adsorption isotherm and pseudo second order kinetic model with the maximum adsorption capacity 107 mg/g at 298K. Spontaneity, feasibility and endothermic nature of adsorption process were shown by the calculation of thermodynamic parameters and adsorbent was regenerated using 0.1M NaOH. The adsorption of dyes onto the adsorbent surface was possibly due to the interactions between dye molecules and functional group on the surface of adsorbent [35]. Activated carbon prepared from date stones by activation with nitric acid was evaluated for their capacity to uptake methyl orange and Maxilon blue from aqueous solutions. The adsorption equilibrium data for methyl orange uptake was well described by Temkin adsorption isotherm while for Maxilon blue uptake was well described by Freundlich adsorption isotherm. Adsorption of methyl orange onto date stone activated carbon is spontaneous and exothermic in nature while Maxilon blue adsorption is endothermic in nature [36]. Batch mode studies for light green dye uptake from aqueous solutions by cationic surfactant hexadecylpyridinium bromide surfactant reveled that adsorption kinetics was well described by pseudo first order kinetic model and Elovich equation and equilibrium data well fitted to Langmuir adsorption isotherm. Calculations of thermodynamics parameters revealed spontaneity and exothermic nature of adsorption process and regeneration of exhausted modified peanut husk was done using 0.01 M NaOH solutions [37]. A commercial coffee waste modified using cationic surfactants cetyl trimethyl ammonium bromide (CTAB) / cetyl pyridinium chloride (CPC) was investigated for the capacity to adsorb methyl orange form aqueous solutions. The study concluded that adsorption equilibrium data and kinetics well fitted to Langmuir adsorption isotherm and pseudo-second order kinetic model. Spontaneity of adsorption process and exothermic nature were concluded from the calculations of thermodynamic parameters. The adsorption of methyl orange onto cationic surfactant modified coffee waste was mainly controlled by electrostatic and hydrophobic interactions [38]. The investigation of watermelon peels as such and modified chemically using NaOH and HNO₃ for the removal of fluoroscien and eosin dyes from aqueous solutions led to conclusion that base treated watermelon peel exhibited highest removal efficiency and chemically unmodified raw watermelon peel possessed least removal efficiency towards fluoroscien and eosin dyes from aqueous solutions. The assessment of thermodynamic parameters revealed physical adsorption, spontaneous and exothermic nature of dye uptake process by the adsorbent [39]. Waste green tea biomass as such and chemically modified using phosphoric acid, sulphuric acid; hydrochloric acid, tartaric acid, sodium hydroxide and hydrogen peroxide were evaluated for the removal of malachite green from aqueous solution. The study concluded that maximum removal efficiency for the uptake of malachite green from aqueous solution was possessed by sulphuric acid modified waste green tea waste and raw green tea waste exhibited least removal efficiency[40]. The evaluation of almond shells for the removal of methyl orange from aqueous solution concluded that equilibrium data and adsorption kinetics well fitted to Langmuir adsorption isotherm and pseudo second order kinetic model. The calculation of thermodynamic parameters proved feasibility, exothermic nature and physical adsorption of dye molecules onto the surface of the adsorbent [41]. The adsorption capacity of prawn shell waste, rice husk, poultry soil waste, apricot seed and tea powder waste were evaluated for their potential to uptake textile dye Levafix Blue CA and leather dye Brown VBR from aqueous solutions. Prawn shell waste exhibited maximum adsorption capacity while tea powder waste exhibited least adsorption capacity for uptake of textile dye Levafix Blue CA and leather dye Brown VBR from aqueous solutions [42]. The utilization of forestery wastes pine cone and oak cups pulps as bioadsorbents for the removal of basic red 18 and acid red 111 dyes from aqueous solution revealed that pine cone and oak cups pulps possessed higher removal efficiency for the uptake of basic compared to acidic dyes. However on modification of these bioadsorbents with nitric acid, for the uptake of basic dyes, adsorption capacity was increased for pine cone while it was reduced for oak cups pulps [43]. The comparative analysis of microwave hydrothermal treated grape peel and conventional hydrothermal treated grape peel for removal of Methylene blue from aqueous solution concluded that microwave hydrothermal treated grape peel exhibited higher adsorption capacity than conventional hydrothermal treated grape peel. The possible mechanism of uptake of Methylene blue by grape peel derived bioadsorbents involves both physisorption and chemisorption which proceed through formation of monolayer of dye molecules on the surface of bioadsorbents [44].



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Sr.no	Dyes	Adsorbent	$Q_m(mg/g)$	Reference
1	Eosin yellow	Teak leaf litter powder	31.64	6
2	Methylene blue	Oiltea shell	64.4	24
3	Methylene blue	Ficus Carica bast	47.62	23
4	Grey BL	Mangifera Indica	33.7	4
5	Methylene blue	Rhus Coriaria L.	151.69	23
6	Maxilon blue GRL	Coconut husk	40.48	25
7	Direct yellow DY 12	Coconut husk	10.58	25
8	Methylene blue	Daucus carota stem	55.5	26
9	Malachite green	Daucus carota stem	43.4	26
10	Methylene blue	Daucus carota leaves	66.6	26
11	Malachite green	Daucus carota leaves	52.6	26
12	Methylene blue	Annona squmosa seed	8.52	27
13	Malachite green	Annona squmosa seed	25.91	27
14	Methylene blue	Cauliflower leaves	149.22	28
15	Methylene blue	Mishwak leaves	200	29
16	Congo red	Groundnut shell charcoal	117.6	30
17	Congo red	Eichhornia charcoal	56.8	30
18	Methylene blue	Punica granatum husk	68.40	31
19	Methylene blue	Eichhornia Crassipes root	128.9	45
20	Victoria blue	Eichhornia Crassipes root	145.4	45
21	Acid green 20	Eichhornia Crassipes stem	200	45
22	BF-4B reactive red dye	Eichhornia Crassipes dried leaves	20.38	45
23	Methylene blue, crystal violet	Alginate fixed Eichhornia Crassipes	86.2	45
24	Acid red 114	Eichhornia Crassipes root	112.34	45
25	Crystal violet	Surfactant modified Eichhornia Crassipes	116.3	45
26	Methylene blue	Finger citron residue based activated carbon	581.40	34
27	Methyl orange	Finger citron residue based activated	934.58	34
28	Congo red	Orange peel powder	107	35
29	Light green anionic dye	Peanut husk	146.2	37
30	Methyl orange	Commercial coffee waste	62.5	38
31	Fluoroscien	Watermelon peels	20.545	39
32	Eosin	Watermelon peels		39
33	Methyl orange	Almond shell	41.34	41
34	Methylene blue	Beach sawdust	10.9	43
35	Methylene blue	Wood shavings	17.9	43
36	Methylene blue	Palm kernel fibre	671.8	43
37	Malachite green	Rice straw	94.3	43
38	Malachite green	Hen feather	9.4	43
39	Malachite green	Luffa cylindrica	29.4	43
40	Methyl violet	Orange peel	11.5	43
41	Rhodamine B	Coir pith	203.2	43
42	Basic blue 41	Canola hull	67.6	43

Table 4: Dye adsorption capacities of various low cost bioadsorbents derived from agricultural waste



B. Effect of pH on dye Removal

The initial pH of the solution dominantly affects the adsorption of dye molecules onto the adsorbent. The existence of inverse relationship between uptake of eosin yellow dye from aqueous solution by teak leaf litter powder and initial pH of the solution was found which concluded that increased removal of eosin yellow at low pH was due increased electrostatic attraction between positively charged binding sites on the adsorbent surface and anionic eosin yellow dye molecules [6]. The maximum removal of Methylene blue by adsorption onto activated carbon prepared from *Ficus Carica* bast was observed at pH 8. Methylene blue is cationic dye and hence in acidic medium positively charged surface of adsorbents tends to oppose the adsorption of cationic adsorbent. While on increasing the pH of the solution, surface of adsorbent acquires negative charge and resulting electrostatic attraction between negatively charged adsorbent surface and cationic dye molecules increases adsorption of Methylene blue [23]. The optimum pH for the removal of Methylene blue and malachite green by *Annona squmosa* seed was around 6 because since on increasing the pH beyond isoelectric point the surface of the adsorbent becomes negatively charged which facilitates the association of positively charged dye molecules through electrostatic forces of attraction [27]. The optimum pH for the uptake of Methylene blue blue by cauliflower leaves was at pH 9 which is because at lower pH the excess H⁺ ions present competes with cationic dye molecules for sorption site; on increasing the pH the surface becomes negatively charged which enable the uptake cationic dye molecules through electrostatic forces of attraction [28].

C. Effect of Adsorbent Dosage

The uptake of Congo red dye by charcoal derived from groundnut shells and *Eichhornia Crassipes* increases from 83-95% and 60-82% respectively on increasing the adsorbent dosage from 0.1 to 1.2 g due increase in availability of adsorption sites and adsorbent surface area with increase in dosage quantity[30]. For the removal of Methylene blue from aqueous solution by adsorption onto *Punica granatum* husk, on increasing the dosage from 0.1 to 0.6 g / 50 ml solution at 298 K and pH 5.0 the dye adsorption increases from 47.8 to 92.6% due to increase in the amount of the surface area and number of vacant binding sites. On further increasing dosage from 0.6 g to 1.0 g / 50 ml solution, no effect on percentage of Methylene blue removal is observed due to aggregation of adsorbent particles at fixed volume of solution [31]. Similar behavior is reported for the removal of methyl orange and Methylene blue from aqueous solution by adsorption onto finger citron residue based activated carbon and uptake of methyl orange by surfactant modified commercial coffee waste [34, 38].

D. Effect Of Initial Dye Concentration

On increasing the initial concentration of Methylene blue from 10g/l to 50 g/l during evaluation of *Punica granatum* husk for its potential to uptake Methylene blue from aqueous solution, the adsorption capacity increases from 9.8 to 42.5 mg/g, due driving force that overcomes mass transfer resistance and also if dye molecule concentration is higher; adsorbent surface is surrounded by more and more dye molecules and hence adsorption occurs more efficiently. Similar behavior is reported for adsorption of Methylene blue onto almond shell [31, 41]. The increase in equilibrium adsorption capacity of Methylene blue onto activated carbon derived from *Ficus Carica* bast up to 50mg/ 100 ml; while with further increase in initial concentration[23]. The percentage removal of crystal violet onto pineapple leaf powder decreases with increase in initial concentration because of availability of limited number of binding sites which becomes saturated certain concentration. So more dye molecules remains unadsorbed in the solution leading to decrease in removal efficiency [46].

E. Effect Of Contact Time

The rapid adsorption of Methylene blue on the almond shell derived bioadsorbents during contact time up to 80 minutes due to large number of vacant dye binding sites being available for adsorption during initial stage which remains unchanged up to 140 minutes as rate of adsorption inclined to slow down leading to equilibrium because of decrease in number of vacant adsorption sites. At initial stages the concentration gradient between the bulk solution and adsorbent external surface is high that facilitates mass transport. Similar behavior is reported for adsorption of Methylene blue onto *Punica granatum* husk and adsorption of crystal violet onto pineapple leaf powder [31, 41, 47]. The equilibrium time for uptake of dyes by some bioadsorbents is as follows:



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Sr.no	Dyes	Adsorbent	Equilibrium time	References
1	Methylene blue	Almond shell	80 min	41
2	Crystal violet	Pineapple leaf powder	120 min	46
3	Crystal violet	Watermelon rind	180 min	46
4	Methylene blue	Punica granatum husk	5 h	44
5	Methylene blue	Ficus Carica bast	90 min	23
6	Methylene blue	Annona squmosa seed	100 min	27
7	Malachite green	Annona squmosa seed	100 min	27
8	Methylene blue	Cauliflower leaf powder	100 min	28
9	Methylene blue	Mishwak leaves	30 min	29
10	Light green anionic	Peanut husk	200 min	37
	dye			
11	Methyl orange	Modified coffee waste	180 min	38

 Table 5: Equilibrium time for various bioadsorbents derived from agricultural waste for dye removal

F. Effect of Temperature

The adsorption of eosin yellow on to teak leaf litter powder increased with increase in the temperature due to increase in adsorption capacity of the adsorbent suggesting endothermic nature of the process[6]. The increase in removal of Congo red by adsorption onto charcoal derived from groundnut and Eichhornia Crassipes with increase in temperature occurs as the result of decrease in the solubility of dye with the increase in temperature, increase in the mobility of large dye ion with temperature, also sufficiently large number of molecules may acquire enough energy to interact with active site of the adsorbent [30]. The decrease in adsorption capacities of Maxilon blue GRL and direct yellow12 onto activated carbon derived from coconut husk with increase in temperature is due increase in solubility of dyes resulting in stronger interaction forces between dyes and solvents than those between dyes and adsorbent. A decrease in adsorption is also related to increase in Brownian movement of molecules in the solution. Also high temperature may lead to cleavage of intermolecular hydrogen bonding between adsorbent and dye molecules. This may also be due to tendency of dye molecule to go to bulk phase from solid phase with the increase in temperature[25].

II. CONCLUSION

The removal of dyes from aqueous solutions by adsorption onto low cost adsorbents derived from agricultural waste is beneficial due its possible regeneration at low cost, sludge free procedure, recovery of adsorbent, more efficient, technically easy and non polluting properties. Different properties of dye solution affecting the uptake of dyes from aqueous solution are pH, initial concentration, dosage of adsorbent, temperature and contact. Similarly, various properties of adsorbent affecting the removal of dyes are specific surface area, pore volume, grain size, pore size distribution and particle size. The evaluation of thermodynamic parameters like entropy, enthalpy and Gibb's free energy predict feasibility and endothermic/ exothermic nature of the adsorption process. Different mechanisms involved in the uptake of dyes from the aqueous solution are electrostatic and hydrophobic interactions, π - π stacking interactions, intra-particle and liquid film diffusion. Agricultural waste derived bioadsorbents are chemically modified using sodium hydroxide, nitric acid, surfactants, organic acids, oxidizing agents, fungal treatments, hydrothermal methods, in order to alter its physic-chemical properties, pore size, surface properties and chemical composition. Although much work is reported for dye removal using bioadsorbents further scaling up the usage of bioadsorbents at industrial scale to demonstrate its effectiveness at large scale must be encouraged. Thus, due to improved capabilities of agricultural waste derived bioadsorbents, they are a sustainable alternative to commercial synthetic bioadsorbents.

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