



Dyes Removal Using Novel Sorbents – A Review

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Efficient and economical treatment for color removal in the effluent of dyeing units and the dyestuff production units have always need an emerging technologies. In general physical methods such as adsorption, ion exchange and filtration/coagulation methods, chemical methods like ionization, Fenton reagent, photo catalytic & biological processes namely aerobic/anaerobic degradation, biosorption are used for dye removal. Adsorption using solid materials (i.e.) adsorbents, considered as an effective process for color removal, because of its higher efficiency over other processes. Researchers made an attempt to use various non-conventional, low-cost, naturally-occurring biomasses as adsorbent, which may be mineral, organic or biological materials. These include fruit peels, seeds, leaves, bark, sawdust, straw, ash sludge and other materials that are available in abundant quantity. The various methods showed the color removal capability of adsorbents; mainly based on the processing methods and the variety of dye. In this review, various dye adsorbents and their capacity for removing the dyes from various effluents is highlighted.

Keywords: Adsorption; dye removal; agricultural residue; adsorbents.

1. INTRODUCTION

From early origins of life to advanced human civilization water is proved to be the most vital

requirement for the survival of living beings [1]. It continuously follows different cycles like transpiration, condensation, evaporation, precipitation and overflow to reach water bodies.

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Over the past decades much attention has been paid for obtaining the safe drinking water; however, one billion people are still short of access to safe drinking water and over 2.5 billion people are short of sufficient water for sanitation [2]. It is expected to reach the world's population of 9 billion by 2050, which may still increase the demand of water. So the appropriate water treatment is necessary for sustaining the life of living beings. Effluents discharged from industries and pesticides used in agricultural lands are the main reasons of water contamination [3]. Even if trace amount of such materials are discharged in to the water bodies, it may cause serious threatening to ecological balance by means of affecting fresh water as well as aquatic animals.

In the industrial scenario, the discharge of large quantity of highly colored waste water poses serious environmental problems. Many processes like textile, printing, rubber, food, leather, plastics, cosmetics, etc. use various dyes [4,5,6] or pigment to color their products, generate large quantity of waste water rich in color as a consequence, which required pretreatment for color before discharge in to the water bodies or publically owned treatment works. Even small amount of dyes can color huge water bodies and hence it is much more economical to pre treat a smaller effluent stream for color at the source than after its dilution into a larger water body. Worldwide annually over 7×10^5 of dyes are produced, from which 100,000 dyes are available commercially [7,8]. Allergic, muta and carcinogenic effects may be caused by these contaminants [9,10]. Dysfunction of kidney, liver, brain, reproductive system and nerves are some effects of dyes on human being [11]. The photosynthesis process is disturbed by means of decreasing the ability of light penetration ability because of lowering the transparency of untreated waste water. Since large amounts of metal complexes are present in the dyes, most of the saleable dyes are treated with difficulty by chemical methods.

Chemical methods such as coagulation or flocculation combined with flotation and filtration, precipitation- flocculation with Fe(II)/Ca(OH)_2 , electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation, electro-flotation or electrochemical processes are used for dye removal. Even though these methods are helpful in dye removal, not much used because of expensive nature and accumulation of concentrated sludge.

These methods are efficient for waste water handling requirement contaminated by various substances, but are not preferred because of various problems of huge electricity demand, abundant requirement of the chemical substances and huge money.

Biological process is considered as the most economical process due to its simple design & operation. But its toxicity problems, low bio degradation of dyes and requirement of larger land area due to diurnal variation makes the biological process as ineffective one [12]. As mixed microbes decolonization needs up to 30 hours to be completed, these biological methods are considered as long period operations. On the other side, few dyes cannot be removed by physical methods such as ion exchange; and for electro kinetic coagulation, high volume of sludge is produced. It has been observed that the biological treatment along with the current conventional biological treatment processes is not proven satisfactory for color elimination [13].

Varieties of processes belonging to the physical methods are used like membrane-filtration techniques (Reverse osmosis, Electro dialysis, Nano-filtration) and different adsorption methods. The main problems of the membrane filtration methods are limited life period, membrane fouling problem and the amount in curred for timely replacement of membranes. It was suggested that adsorption is an effective process for the elimination of pollutants present in the wastewater. Hence, adsorption has been considered as a most suitable process over other processes for reuse of water in terms of money, simple design, easy functioning and action against toxic substances [14]. The different technologies used for color removal are shown in Table 1. In addition, proper adsorption has the potential to generate a best in class treated waste water [15]. Adsorption has been used extensively in industrial process for separation and purification not only dyes and pigments, but also for other contaminants such as heavy metal impurities from waste water or sewage [16,17,18, 19,20,21,22]. The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption processes. The accumulation of adsorbates at gas-solid or liquid-solid interface is called adsorption phenomena [23]. In most cases, adsorption is reversible because of weak Van der Waals bonds between adsorbent and adsorbate [24]. Isotherm models are fundamental concepts that deal with

adsorption science. They explain how adsorbate and adsorbent interact to each other; and also by these models, the adsorption capacity can be calculated [25,26]. While chemical treatments produce foul odor and byproducts, and are expensive; adsorption phenomena is of interest

for dyes removal because of its low cost and flexibility in design and also because this process does not produce any harmful substances after removal of the target compounds. But the main challenge is that selection of suitable, renewable and economical adsorbents [27].

Table 1. Showing different technologies with their advantages and disadvantages for color removal [28]

Process	Technology	Advantages	Disadvantages
Chemical Processes	Fenton reagent.	Effective process and cheap reagent.	Sludge production and disposal problems
	Ozonation	No production of sludge.	Half-life is very short (20 min) and high operational cost.
	Photo catalyst	Economically feasible and low operational cost.	Degrade of some photo catalyst into toxic by-products.
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Aerobic degradation	Efficient in the removal of azo dyes and low operational cost.	Very slow process and provide suitable environment for growth of microorganisms.
	Anaerobic degradation	By-products can be used as energy sources	Need further treatment under aerobic conditions and yield of methane and hydrogen sulfide.
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals Required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective Bio adsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms	Slow process, performance depends on some external factors (pH and salts)

Even though variety of adsorbents are used for the adsorption process, the selection of suitable adsorbent depend on the factors like concentration and type of micro pollutant, its efficiency/cost ratio, adsorption capacity, high selectivity for a large volume of water. In addition the selected adsorbents should be non-toxic, less cost, easy regeneration capability, easy recovery from filters, readily available, and should lead to zero waste/sludge [29]. The most common commercially available adsorbents are activated carbon, ion exchange materials, biosorbents, zeolite, bentonite clay, etc. Among these, Commercial activated carbon is considered as a very effective adsorbent for dye removal; but due its high cost, researchers concentrate on various alternative and low cost adsorbents such as bio sorbents, natural materials, agricultural wastes and industrial by-products. These include silica gel, clays, sawdust, peat, and fly ash [30,31]. The present review paper highlights the various adsorbents that are used for effective removal of dyes from industrial waste water.

1.1 Dyes and its Classification

Dyes are chemicals, which on binding with a material will give color to them. Dyes are ionic, aromatic organic compounds with structures including aryl rings, which have delocalized electron systems. The color of dye provided by the presence of a chromophore (OH, NH₂, NHR, NR₂, Cl and COOH) group. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalized electrons. The Chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogen chromophore structure along with an auxochrome (NO₂, NO, N=N). The presence of ionising groups known as auxochromes results in a much stronger alteration of the maximum adsorption of the compound and provides a bonding affinity toward the fibre. Without any chemical treatment dyes are derived from plant sources such as indigo and saffron, insects are cochineal beetles and lab scale insects, animal sources are derived from some species of mollusks or shellfish and minerals are ferrous sulfate, ochre [32]. Dye bearing effluents from these industries are characterized by its high colour, organic content and hazardous as well. Dyes can be produced from natural or synthetic sources as shown below.

1.1.1 Natural dyes

Natural dyes are organic compounds used to colour various products. In Prior to the year of 1856, natural dyes are extracted from plants, animals, insects and minerals sources. Natural dyes are such as Turmeric, Weld, Onion, Jackfruit, henna, eucalyptus are used in the early textile industry. Due to the increase in population and industrial activities, natural dyes do not meet the industrial demand and their applications have been limited mainly in food industry. The most common natural dyes used in textile industry are presented in Table 2 along with their scientific names and chemical structures.

1.1.2 Synthetic dyes

The first synthesis dye was discovered by William Henry Perkin in 1856. Dye effluents are produced because dyes do not have a complete degree of fixation to fiber during dyeing and finishing processes [34]. Dye based effluents can cause a serious hazards to the water stream and environment due to their synthetic origin and complex molecular structures which decrease their ability to biodegrade. There are various types of dyes used in various industries such as acid dyes, reactive dyes, basic dyes, azo dyes, direct dyes, vat dyes and disperse dyes [35]. All dyes are water soluble except disperse dyes and vat dyes. All dyes contain traces of metals such as copper, zinc, lead, chromium and cobalt in their aqueous solution except vat and disperse dyes. Dyes are broadly classified into cationic, anionic and non-ionic dyes. Anionic dyes include various dyes' groups such as acid dyes, reactive dyes, azo dyes and direct dyes while cationic dyes are the basic dyes. Dye's classifications and their applications are presented in Table.3. Classification of dyes based on their nature and their toxicity are given in Tables 4 & 5.

1.2 Adsorbents for Dye Removal

Dye removal can be performed by different types of adsorption such as batch methods, fixed-bed-type processes, pulsed beds, moving mat filters and fluidized beds for getting experimental data as well as for industrial purposes. However batch-type contact and fixed bed-type processes are frequently used. Fig. 1 illustrates the Schematic representations of two main schemes used for adsorption of pollutants from wastewaters: batch process and continuous process.

Table 2. The common natural dyes used in textile industry [33]

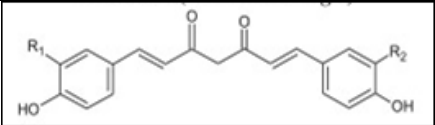
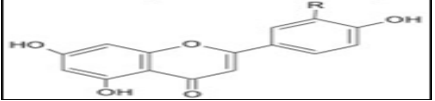
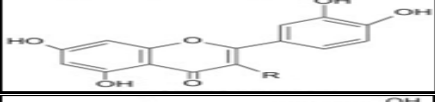
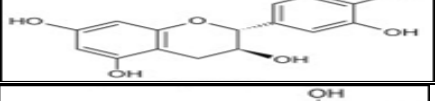
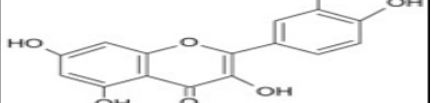
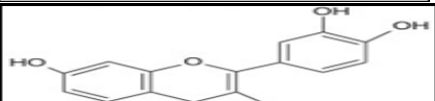
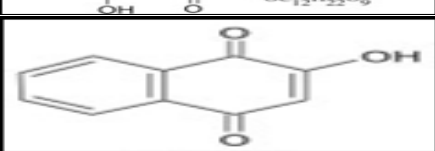
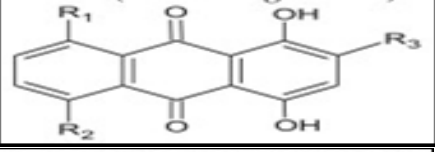
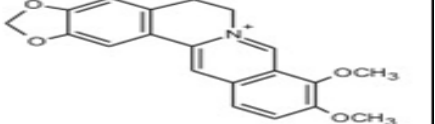
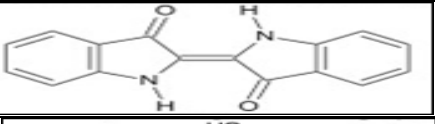
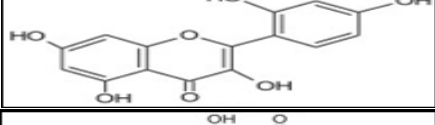
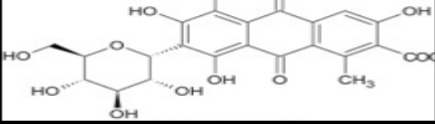
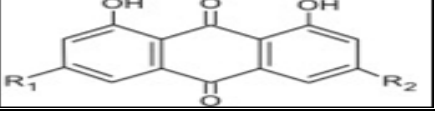
Natural dyes	Scientific names	Structure
Turmeric	Curcuma Longa	
Weld	Reseda Luteola	
Eucalyptus	Eucalyptus globules	
Cutch	Acacia Catechu	
Onion	Aliumcepa	
Flossophorae	Sophora japonica	
Henna	Lawsoniainermis	
Teak	Tectona grandis	
Berberry	Berberisaristata	
Indigo	Indigofera tinctoria	
Jackfruit	Artocarpus heterophyllus	
Cochineal	DacylopiusCoccus	
Indian Rhubarb	Rheum emodi	

Table 3. Classification of synthetic dyes based on applications [36,37,38]

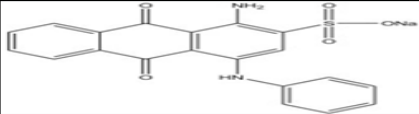
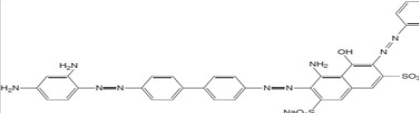
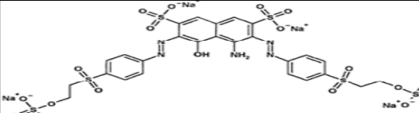
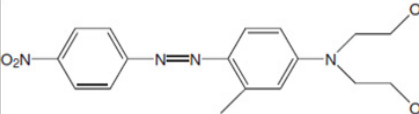
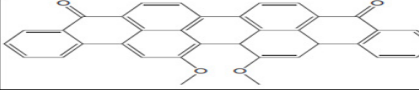
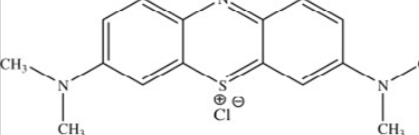
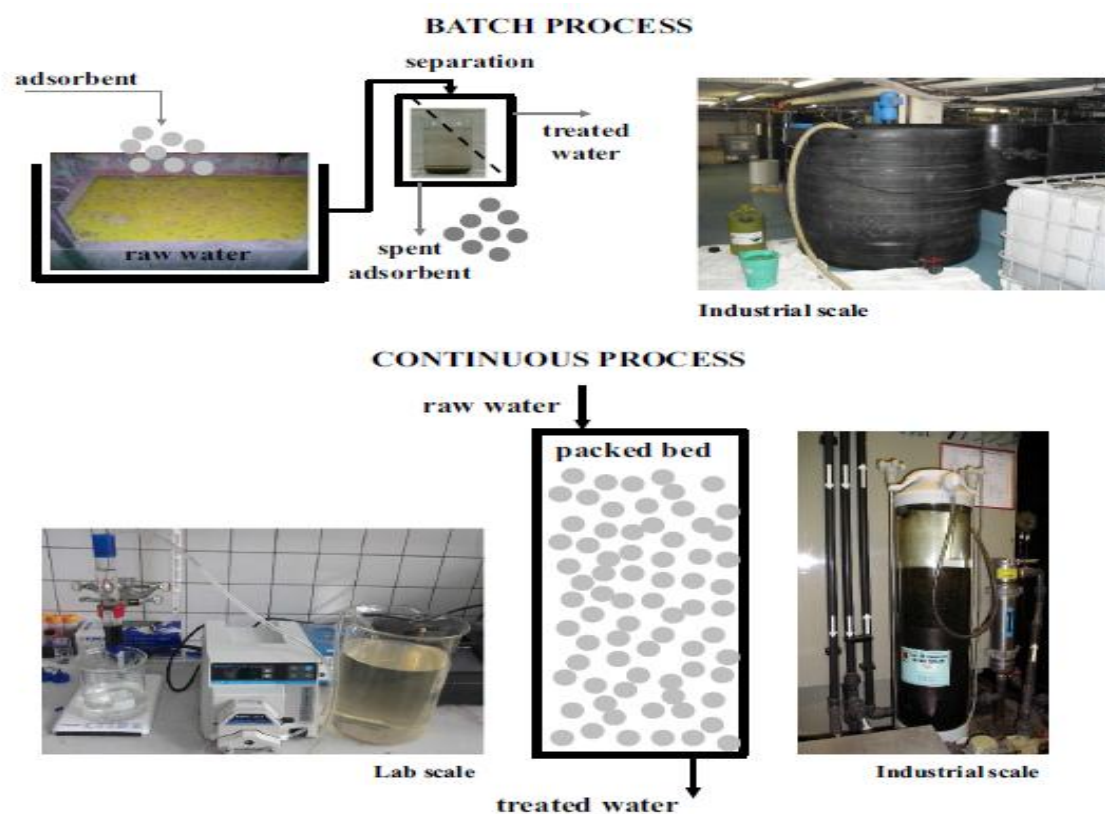
Dyes	Examples of dyes	Chemical structure's example	Applications of dyes
Acid dyes	Congo red Methyl (orange and red) Orange (I,II) Acid (blue, black, violet, yellow)		Wool Silk Nylon (Polyamide) Polyurethane Fibers
Direct dyes	Martius yellow Direct black Direct orange Direct blue Direct violet Direct red		Cotton Wool Flax Silk Leather in (alkaline or neutral bath)
Reactive dyes	Reactive red Reactive blue Reactive yellow Reactive black Remazol (blue, yellow, red, etc)		Cellulosic fibres Wool Polyamide
disperse dyes	Disperse blue Disperse red Disperse orange Disperse yellow Disperse brown		Polyamide fibers Polyesters Nylon Polyacrylonitriles
Vat dyes	Indigo, Benzanthrone Vat blue Vat green		Wool Flax Wool Rayon fibers
Basic dyes	Methylene blue Basic red Basic brown Basic blue Crystal violet Aniline yellow Brilliant green		Polyester Wool Silk Mod-acrylic Nylon

Table 4. Classification of dyes based on their nature [39]

Sl. No	Class	Application	Examples
1	Acid dyes	Nylon, wool, silk, modified acrylics, paper, leather, food, inkjet printing and cosmetics.	Acid red 88, Acid red 18
2	Cationic (Basic) Dyes	Poly acrylonitrile, paper, modified polyesters, modified nylons, cation dye able polyethylene terephthalate, wool, silk, tannin mordanted cotton and medicine.	Crystal Violet, Methylene Blue, Safranin, Basic fuschin
3	Disperse Dyes	Nylon, polyester, cellulose, acrylic fibers and cellulose acetate.	Disperse Red 1, Disperse Orange 37
4	Direct Dyes	Rayon and cotton, leather, paper and nylon.	Congo Red, Brilliant Blue, copper blue 2R
5	Reactive Dyes	Wool, nylon, cotton and other cellulosic.	Reactive Black 5, Reactive Orange 16
6	Solvent Dyes	Gasoline, plastics, oils, lubricants and waxes.	Solvent Red 1, Solvent Red 49, Solvent Red 24, Solvent Red 111
7	Sulfur Dyes	Cotton and rayon, paper, leather, silk and wood.	Sulfur Brilliant Green, Sulfur black 1
8	Vat Dyes	Cotton, rayon and wool.	Vat red 10, vat violet 13 and vat orange 1.

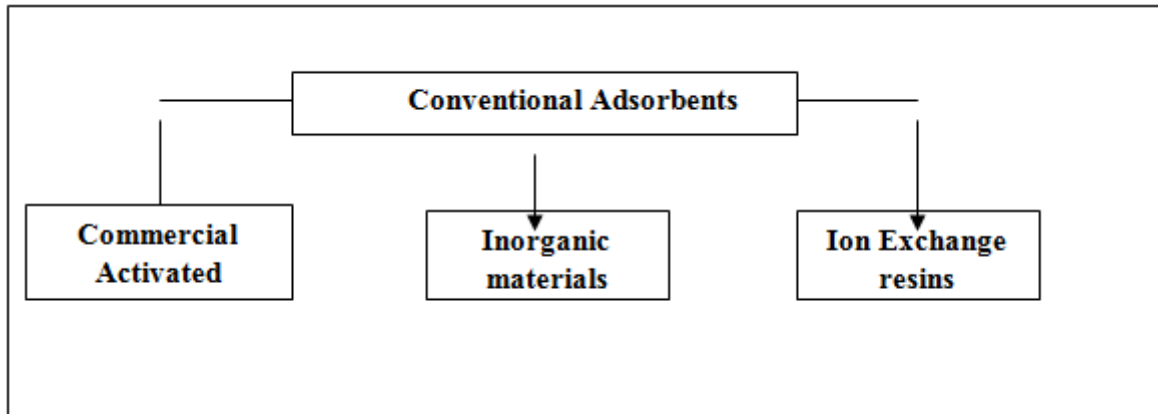
Table 5. Toxicity of some dyes

SI.No	Name	LD ₅₀ (mg/kg rat)	LD ₅₀ (mg/kg rat)
1	Malachite green	275	[40]
2	Acid orange 165	60	[41]
3	Acid orange 165	100	[41]
4	Basic Blue 81	205	[41]
5	Basic Violet 16	90	[41]
6	Basic Yellow 21	171	[41]
7	Direct Orange 62	150	[41]

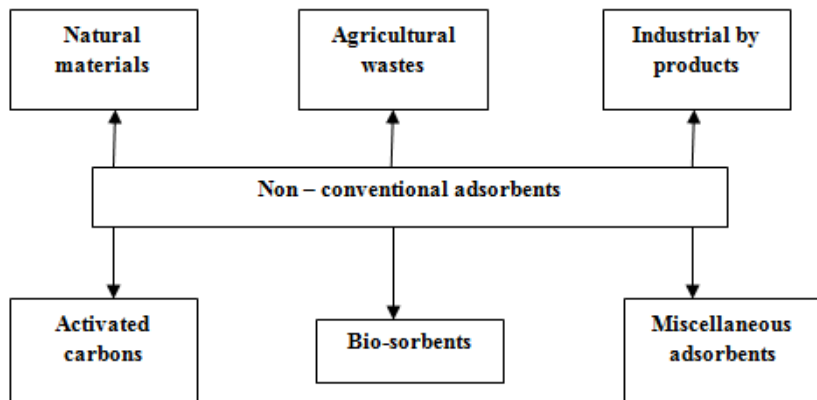
**Fig. 1. Schematic representations of two main schemes used for adsorption of pollutants from wastewaters: batch process and continuous process**

Higher residence times and better heat and mass transfer characteristics are other advantages of employing fixed-bed columns for industrial adsorption processes than batch reactors. But batch methods are also widely preferred because of cheap and simple to operate and, consequently, often favored for small- and medium-size process applications using simple and readily available mixing tank equipment. Simplicity, well-established experimental methods, and easily interpretable results are some of the main reasons frequently evoked for

the extensive use of these methods. Another interesting advantage is the fact that, in batch systems, the parameters of the solution/effluent such as contact time, pH, strength ionic and temperature can be controlled and/or adjusted. The various types of adsorbents used in the reactors are shown in Fig 2. and also the adsorbents used for removal of dyes from aqueous solutions & recent researches on dye adsorption by different adsorbents are reported in Table 6.



- | | | |
|---|--|--|
| <ul style="list-style-type: none"> - Wood - Peat - Coconut Shells - Coals (anthracite, bituminous, lignite...) | <ul style="list-style-type: none"> - activated alumina - Silica gel - Zeolites - Modular Sieves | <ul style="list-style-type: none"> - Polymeric organic resins - non – porous resins - Porous crosslinked polymers |
| <ul style="list-style-type: none"> - Inorganic materials (clinoptilolite) - Silicious materials (alunite, perlite, dolomite, glasses..) - Clays (bentonite, Kaolinite, diatomite, sepiolite Vermiculite) | <ul style="list-style-type: none"> - Saw dust - bark - Solid wastes date pith, corn cob, wheat straw, Orange Peel...) | <ul style="list-style-type: none"> - fly ash - red mud - Sludge - metal hydroxide - Sludge |



- | | | |
|--|---|--|
| <ul style="list-style-type: none"> - Agricultural solid waste (fruit stones, bagasse, coir pith, date pits, maize cob) - Industrial by products (PET Bottles, waste tyres, sewage sludge, newspapers..) | <ul style="list-style-type: none"> - Biomass (fungi, Yeasts bacteria, algae) - Peat - Chitin/chitosan - Other Polysaccharides and their derivatives (cellulose, starch cyclodextrins, alginates...) | <ul style="list-style-type: none"> - Cotton waste - Cucurbituril - Calixarenes - Hydrogels |
|--|---|--|

Table 6. Adsorbents used for removal of dyes from aqueous solutions

Adsorbent	Dye investigated	Max. adsorption capacities (mg/g)	Reference
Grass waste	Methylene blue	457.640	[42]
Luffa cylindrical fibres	Methylene blue	47	[43]
<i>Caulerparacemosa var. cylindracea</i>	Methylene blue	3.423	[44]
Solid waste of soda ash plant	Reactive red 231	667	[45]
Chitosan bead	Malachite green	93.55	[46]
Biomass flyash (FA-BM)	Reactive black 5	4.38	[47]
Biomass fly ash (FA-BM)	Reactive yellow 176	3.65	[47]
Castor seed shell	Methylene blue	158.73	[48]
Chitosen-based adsorbent	Basic blue 3	166.5	[49]
Untreated desert plant	Methylene blue	23	[49]
Pyrolized desert plant	Methylene blue	53	[49]
Chemically activated desert plant	Methylene blue	130	[50]
Untreated guava leaves	Methylene blue	295	[51]
Yellow passion fruit waste	Methylene blue	44.70	[52]
Oil palm trunk fibre	Malachite green	149.35	[53]
Sunflower seed hull	Methyl violet	92.59	[54]
Broad bean peels	Methylene blue	192.7	[55]
Soy meal hull	Direct red 80	178.57	[56]
Soy meal hull	Direct red 81	120.482	[56]
Soy meal hull	Acid blue 92	114.943	[56]
Soy meal hull	Acid red 14	109.89	[56]
Citrus documana	Reactive red 2	0.608 mg/g	[57]
Citrus medica	Reactive red 2	0.580 mg/g	[57]
Citrus aurantifolia	Reactive red 2	0.566 mg/g	[57]
Orange peel (<i>Citrus sinensis</i> L)	Remazol brilliant blue	11.62 mg/g (20°C), 10.70 mg/g (30°C), 8.61 mg/g (40°C), 6.39 mg/g (50°C), 5.54 mg/g (60°C)	[58]
Mosambi peel	Erichrome black T	90% (Initial dye concentration 50 mg/g & adsorbent dose 4 g/L)	[59]
Palm nut shell carbon	Dark green PLS	0.84 mg/g	[60]
Cashew nut shell carbon	Dark green PLS	1 mg/g	[60]
Broom stick carbon	Dark green PLS	0.63 mg/g	[60]
Coconut shell char	Rhodamine-B	41.67 mg/g	[61]
Coir pith char	Coomassie brilliant	31.84 mg/g	[62]
Palm shell activated carbon	Reactive red 3 BS	7 mg/g	[63]
Palm shell powder	Methylene blue	121.5 mg/g	[64]
	Rhodamine 6G	105 mg/g	
Sugarcane bagasse	Reactive orange	3.48 mg/g	[65]
Sugarcane bagasse (ZnCl ₂ treated)	Reactive orange	2.83 mg/g	[65]
Sugarcane bagasse (H ₃ PO ₄ treated)	Reactive orange	1.8 mg/g	[65]
Sugarcane bagasse flyash	Remazol Black B	16.42 mg/g	[66]
	Remazol brilliant blue R	32.468 mg/g	[66]
	Remazol Brilliant red	18.282 mg/g	[66]
Sugarcane bagasse	Basic blue 3	37.59 mg/g	[67]
	Reactive orange 16	34.48 mg/g	[67]
Sugarcane dust	Basic violet 1	50.4 mg/g	[68]
	Basic violet 10	13.9 mg/g	[68]

Adsorbent	Dye investigated	Max. adsorption capacities (mg/g)	Reference	
Rice hull	Basic green 4	20.6 mg/g	[68]	
	Basic blue 3	14.68 mg/g	[69]	
	Reactive orange 16	6.24 mg/g	[69]	
Rice husk carbon	Congo red	10 to 99% (Initial dye concentration 25 ppm & adsorbent dose 0.08 g/L)	[70]	
Saw dust	Ethylene blue	87.7 mg/g (natural saw dust). 188.7 mg/g (treated saw dust)	[71]	
Beech wood saw dust	Direct orange	2.78 mg/g	[71]	
	Acid green 20	7.81 mg/g	[71]	
	Aid orange 7	5.06 mg/g	[71]	
Activated sludge	Rhodamine-B	5.121 mg/g (5°C), 4.847 mg/g(15°C), 4.456 (25°C), 3.725 mg/g (45°C)	[72]	
Sewage sludge activated carbons	Reactive dye	33.5 mg/g	[73]	
Granular activated sludge	Acid orange 7	92% (at dye loading rate of 590 mg/L.day)	[74]	
Fermentation waste (<i>Corynebacterium glutamicum</i>)	Reactive black 5	169.5 mg/g (20°C), 185.2 mg/g (40°C)	[75]	
Sewage treatment plant sludge	Rhodamine B	5.121 mg/g(5°C), 4.847 mg/g (15°C), 4.456 mg/g (25°C), 3.725 mg/g (45°C)	[75]	
Water treatment plant sludge	Reactive orange 16	47.0 mg/g	[76]	
Sewage treatment plant sludge	Reactive orange 16	114.7 mg/g	[77]	
Anaerobic digestion sludge	Reactive orange 16	86.8 mg/g	[77]	
Land fill sludge	Reactive orange 16	159.0 mg/g	[77]	
Brewery yeast dead cell	Reactive orange 16	0.604 mg/g (pH 3), 0.090 mg/g (pH 7), 0.50 mg/g (pH 10)	[77]	
Baker's yeast cells	Acridine orange	82.8 mg/g	[78]	
	Aniline blue	430.2 mg/g		
	Malachite green	19.6 mg/g		
	Safranin O	90.3 mg/g		
	Crystal violet	85.9 mg/g		
Fungus	Reactive red 198	1.03 x 10 ⁻⁴ mol/g	[79]	
Fungal biomass (<i>Aspergillus niger</i>)	Acid blue 29	64.7 mg/g	[80]	
	Disperse red 1	0.1 mg/g		
	Congo red	1.1 mg/g		
	Basic blue 9	8.9 mg/g		
Gulmohor leaves	Methylene blue	120 mg/g (293 K), 178 mg/g (303 K) and 253 mg/g (313 K)	[81]	
		Malachite green	444.44 mg/g	[82]
		Methylene blue	454.5 mg/g	
Agave (Americana (L) leaves fibres)	Alpacide yellow	16.97 mg/g (20°C), 15.79 mg/g (30°C) and 21.41 mg/g	[83]	

Adsorbent	Dye investigated	Max. adsorption capacities (mg/g)	Reference
Pandanus leaves	Congo red	(50°C) 21.491 mg/g (30°C), 20.267 mg/g (40°C), 20.069 mg/g (50°C), 18.928 mg/g (60°C)	[84]
Pandanus leaves	Malachite green	9.737 mg/g (30°C), 9.624 mg/g(40°C), 9.633 mg/g (50°C), 9.569 mg/g (60°C)	[85]
Tendu (<i>Diospyros melanoxylon</i>) leaf	Crystal violet	67.57- 22.47 mg/g depending on processing of adsorbent.	[86]
Tuberose sticks	Methylene blue	80% (at pH 11, adsorbent dose 1 g/L, 40 mg/L dye concentration)	[87]
Flame tree (<i>Delonix regia</i>) pods	Crystal violet	16.70 mg/g	[88]
Muntingiacalabura Leaves	Methylene blue	20 mg/g	[89]
	Methylene red	58 mg/g	
	Malachite green	32 mg/g	
Water hyacinths (<i>Eichhornia crassipes</i>)	Acid and reactive dyes	Higher N2 percent of hyacinths showed higher adsorption capacities	[90]
Seaweed (<i>Luminaries sp.</i>)	Reactive black 5	101.5 mg/g	[91]
Sea grass leaf sheaths	Reactive red 228	80% dye removal efficiency at pH 5	[92]
Aquatic plant (<i>Hydrilla verticillata</i>) <i>Malachite green</i>	Malachite green	91.97 mg/g	[93]
Teak tree bark	Methylene blue	333.33 mg/g	[94]
	Methylene blue	38.46 mg/g	[95]
Oak saw dust			
Barley straw	Methylene blue	27.72 mg/g	[96]
Wheat straw	Methylene blue	17.54 mg/g	[96]
Oat straw	Methylene blue	8.34 mg/g	[96]
Papaya seeds	Methylene blue	250.0 mg/g (esterified adsorbent) 200 mg/g (natural sorbent)	[97]
Annona squamosa seeds	Methylene blue	8.52 mg/g	[98]
	Methylene red	40.8 mg/g	
	Malachite green	25.91 mg/g	
Hen feathers	Tartrazine (azo dye)	47% (30 °C), 52% (40 °C), 55% (50 °C)	[99]
Chitosen	FD & C Red n° 40 dye	1065.8 µmol/g (308 K), 1061.4 µmol/g (318 K), 800.8 µmol/g (328 K),	[100]

Adsorbent	Dye investigated	Max. adsorption capacities (mg/g)	Reference
		508.5 μ mol/g (338 K)	
Cotton fibres	Reactive red 120	11.63 mg/g	[101]
	Reactive black 5	6.22 mg/g	
Commercial activated carbon	Turquoise blue QG	140.14 mg/g	[102]
	reactive bye		

1.3 Recent Researches on Dye Adsorption by Different Adsorbents

In 1550 Egyptians used adsorption process for removal of unwanted compound, they adsorbed odorous from wounds and intestines by using charcoal as an adsorbent. The same charcoal was used by Phoenicians to purify water in 460 BC [103,104]. In 1912 Chapman and Siebold published very first article for separation of dye molecules from water by using adsorption process [105].

1.3.1 Zeolites

Linoptilolite, a heulandites group zeolite is easily and commonly used among 40 different naturally available zeolites. ~90% of Rhodamine B dye was adsorbed by 3A zeolite from industrial wastewater [106]. In spite of its attractiveness due to cheapness, high surface area and high ion-exchange capability, high different cavity structure and high porous makes the sorption mechanism in zeolites are very complex [107,108,109]. Trace element such as phenols, heavy metals, etc. can also be removed by zeolites.

1.3.2 Alumina

Alumina having granule appearance with surface area of 200-300 m²/g can be synthesized in various shapes. Disperse dyes from water was adsorbed by alumina [110]. Alumina was also analyzed for removal of various industrial dyes like bromophenol blue, malachite green, Methylene Blue, Methyl Blue, Methyl Violet, phenol red and eriochrome black T by varying the parameters such as different shaking times, amount of adsorbent used, temperature and pH. The optimum values were found to be 0.2 g as adsorbent dosage with a shaking time of 40 minutes at lower pH. Langmuir adsorption isotherm and pseudo second order kinetics fitted well with this study [111].

1.3.3 N. Bentonite

MB adsorption was increased with increasing temperature using bentonite. Redlich-Peterson

adsorption isotherm was found to be fit among Langmuir, Freundlich, and Redlich-Peterson isotherms during the analysis of equilibrium adsorption data. The endothermic, increasing randomness at the solid/liquid interface and spontaneous nature during the of adsorption were denoted by positive value of standard enthalpy, standard free energy and negative value of standard entropy [112].

1.3.4 Silica gel

Colloidal silicic acid coagulation produces Silica gel, which is a porous, non-crystalline granule. The surface area of it booms expeditiously rather than alumina and reaches to 900 m²/g. A maximum adsorption capacity for modified silica gel was reported as 11.1 mg/g for removal of sulfur dyes from aqueous solutions [113].

1.3.5 Activated carbon

Oldest well-known adsorbent produced from eco-friendly and environmental friendly materials such as coconut shell, lignite, wood, coal, etc., have been used instead of high cost commercial activated carbon. It is also very effective because of its high surface area [114,115].

Methylene blue was adsorbed using untreated and KOH treated activated carbon (30%-ACKOH) by varying the parameters like contact time, solution pH and adsorbent dosage. the results showed that both adsorbents at 50 and 100 ppm were fairly similar with the capacity uptake of 80-90% but the contact time was reduced (i.e 120 mins) in the case of KOH treated activated carbon than the untreated activated carbon (i.e. 180 mins) and adsorption increased with increase in pH value and adsorption dosage [116]. Another study MB was removed by Activated carbon prepared from palm kernel shell showed 99.7% removal of Methylene Blue dye at 25°C and at 20 ppm initial concentration [117]. Similarly Methylene Blue adsorbed was found to be 62.5 mg/g at room temperature at the pH of 7 and adsorbent size of 125-250 μ m by epicarp of Ricinus communis [118].

The coconut coir activated carbon showed higher capacity for adsorption of Remazol Red F-3B than the commercially available activated carbon compared with Remazol Blue [119]. Maximum color removal was attained at the low pH of 1-3 in 3 hours time. Activated carbon prepared by chemically activating bamboo waste precursor using H_3PO_4 which was used to study the adsorption of C.I. Reactive Black 5 (RB5) onto its surface [120]. Activated carbon from mango peels using K_2CO_3 was also found effective for adsorption [121].

1.3.6 Removal of dye by Mesoporous activated carbon from tyre rubber

Minerals such as Ca, K and Na, which affect the reactivity of gas-solid reactions in the subsequent physical activation process (CO_2 as activating agent) whereas those which possess high mesopore volume up to 0.855 cc/g which has been proved more favourable to the adsorption process for the removal of large absorption of dye from the aqueous solution can be effectively removed by activated carbons produced from tyre rubber [122]. It was also found the amount adsorbed by the tyre char is inversely proportional to the total surface area when compared with a commercial carbon, having size like for the Acid Yellow 117 dye (MW= 848 g/mol), which reveals that factors other than total surface area are involved in the adsorption potential of the tyre chars [123].

Research studies proved the uses of treated sewage sludge for separation of dyes from polluted water and waste water [124, 125, 126, 127, 128, 129]. Pyrolyzed sewage sludge was chemically activated to produce activated carbon. The main advantages of such type of materials were studied mainly by liquid-phase adsorption by using indigo carmine, phenol and crystal violet as adsorbents. Three prepared activated carbon of various particle sizes, were used ASS-g1 (particle diameter < 0.12 mm), ASS-g2 (0.12 mm < particle diameter < 0.5 mm) and PSS-g2 (0.12 < particle diameter < 0.5 mm). Indigo carmine dye adsorption has shown lesser (Q_{max} 60.04 mg/g using AAS, 54.8 mg/g using ASS and 30.8 mg/g using PPS) than Crystal violet dye adsorption higher (Q_{max} 263.2 mg/g using AAS, 270 mg/g using ASS and 184 mg/g using PPS). They suggested and proposed that separation of organic pollutants from aqueous streams by using activated carbons from sewage sludge.

In an agitated batch adsorber, activated carbon, raw kaolinite and montmorillonite were used for the removal of acid red 183 from aqueous solution. At 250°C the adsorption capacity for CAC (commercial activated carbon), HAC (activated carbon obtained from hazelnut), KC (raw kaolinite) and MC (montmorillonite) capacity was found to be 1495, 111, 29 and 19 mg/g at respectively [130]. Removal of dyes and metal ions from aqueous solution by the Activated carbons prepared from waste cassava peel impregnated with H_3PO_4 showed higher efficiency than the heat treated materials. The removal of a basic dye, Rhodamine – B, by using tapioca peel activated carbon as an adsorbent was also studied [131].

Efficiency of bamboo-based activated carbon was improved by treating it with KOH and CO_2 along with the simulation studies for the effect of agitation time and concentration of dye were also carried out. The equilibrium data for Methylene blue adsorption well fitted to the Langmuir equation, with maximum monolayer adsorption capacity of 454.2 mg g⁻¹ [132].

1.3.7 Wood-shaving bottom

Wood-shaving bottom ash / H_2SO_4 and Wood-shaving bottom ash/ H_2O adsorbents were made by treating Wood-shaving bottom ash with 0.1 M H_2SO_4 and water respectively; to increase the adsorption capacity. The effects of various parameters on adsorption such as initial pH of solution, contact time, dissolved metals and elution studied. The maximum dye adsorption capability of WBA/ H_2SO_4 and WBA/ H_2O achieved from a Langmuir model at 30°C were 24.3, 29.9, and 41.5 mg l⁻¹ correspondingly [133].

1.3.8 Adsorbents from industrial by-products

Recently, industrial development produced huge amount of solid waste as by-products. Some of these are reused. These industrial wastes are almost free of cost and cause a disposal problem [134]; therefore, they can be reused as a cost-effective adsorbent. Metal sludge, fly ash, and red mud are some commonly used low-cost adsorbents obtained from industrial waste for the removal of dyes [135, 136, 137].

1.3.9 Metal hydroxide sludge

In an electroplating industry metal hydroxide-based sludges are produced in dried form by the precipitation of metal ions and showed high

adsorption capacity for azo reactive (anionic) dyes from industrial waste water [138].

1.3.10 Fly ash

Fly ash is a residue that results from the combustion of coal in thermal power plants. The major components of fly ash are alumina, silica, iron oxide, calcium oxide, magnesium oxide and residual carbon. Its abundance availability and the presence of pozzolanic particles that react with lime in the presence of water to form cementation calcium-silicate hydrates prefers the use of fly ash over other adsorbents [139].

The fly ash adsorbent is found to contain 60.10% SiO₂, 18.60% Al₂O₃, 6.40% Fe₂O₃, 6.30% CaO, 3.6% MgO. The values of surface area, porosity, and bulk density of the adsorbent are 40.16 m²/g, 0.43 and 3.51 g/cm³ respectively [140]. The fly ash adsorbent was used for the removal of various dyes like Methylene blue, Malachite green and Rhodamine – B, from aqueous solutions. The high colour removal percentages are 93%, 89% and 77% for the dyes, Methylene blue, Malachite green and Rhodamine – B, respectively. The adsorption on dyes, Malachite green and Methylene blue was studied on two different samples of fly ash, fly ash I and II [141]. They have concluded that the maximum color removal was attained with fly ash containing high carbon content. Experiments of continuous mode sorption were also carried out to remove methylene blue from its aqueous solutions in hydro cyclone equipment. At an adsorbent dosage of 900 ppm and the pH condition of 6.75 maximum removals of 58.24% was observed for an initial methylene blue concentration of 65 ppm [142].

Congo red dyes can be removed by using the Calcium-rich fly ash under various conditions. Experimental studies proved that the maximum adsorption obtained and it was between 93%-98% [143]. It was also found that methylene blue and basic dye from waste water can be removed by using treated and non-treated fly ash. The adsorption capability for non-treated fly ash presented an adsorption capacity of 1.4 × 10⁻⁵ mol/g, while treated fly ash was found to be 2.4 × 10⁻⁵ mol/g [144]. Porous unburned carbon in the fly ash can be responsible for the adsorption of dye [145,146,147]. Fly ash from bagasse strongly adsorbed Orange-G (OG) at pH 4 and Methyl violet (MV) at pH 9.0. The percentage of dye removal was higher at low initial concentration and increased in amount of adsorbent used. The adsorption data have been

correlated with Freundlich, Langmuir, Redlich–Peterson, Dubinin–Radushkevich and Temkin adsorption models. The authors observed that the Freundlich isotherm gave the best correlation for the adsorption of Orange-Green-bagasse fly ash system and Redlich–Peterson isotherm better fits the Methyl violet-bagasse fly ash system. The adsorption of Methylene violet and Orange Green followed pseudo-second-order kinetics [148].

1.3.11 Red mud

Red mud is another industrial by-product [149,150,151], which is produced during the production of Alumina as bauxite processing residue. It was observed that the capacity of waste red mud which can be used effectively for the removal of dye from wastewater [152], and found maximum adsorption of dye removal occurred at pH 2. Waste red mud was also used for the removal of Congo red from aqueous solution [150] with the maximum adsorption capacity of 4.05 mg/g, the basic dye methylene blue with the maximum adsorption capacity of 7.8 × 10⁻⁶ mol/g [153] and congo red by using Langmuir isotherm model [154]. Both Langmuir and the Freundlich models were studied for the removal of rhodamine B, methylene blue, and fast green dyes from waste water. The percentage of removals for rhodamine B is 92.5, methylene blue is 94.0, and fast green is 75.0 [155].

1.3.12 Spent Brewery grains

Adsorption of acid dyes (Acid Yellow – AY 17 and Acid Blue – AB 25) onto spent brewery grains (SBG) from brewery industry waste was studied by varying the parameters were studied like, the influence of time, pH, adsorbent dosage, temperature and initial dye concentration. It was found that the uptake was the maximum at pH value of 2 and thereafter the uptake decreased with increase in pH for both the dyes. Colour removal was found to increase with increase in biosorbent dosage and time, while it decreased with decrease in dye concentration and temperature [156].

Batch mode adsorption experiments were carried out for removing Basic blue 3, Basic red 22 and Basic black 9 from aqueous solutions using sewage treatment plant biosolids (sludge), by varying contact time, initial dye concentration, initial adsorbent dosage, agitation rate, temperature and pH. The results revealed that

the adsorption capacity of basic dyes was higher (22-24 mg/g) with the lower values of the temperature (25-30°C), adsorbent dosage (0.5-0.75% w/v), higher values of the initial pH (8-9) and agitation rate (150-200 rpm) at 2 h of operation [157].

1.3.13 Clay based adsorbents

From the earliest days of civilization Clays, made up of the colloidal fraction of soils, sediments, rocks and water [158] are found to be effective for removing pollutants from wastewater. The ions present in the clay surface such as Ca^{2+} , Mg^{2+} , H^+ , K^+ , NH_4^+ , Na^+ , SO_4^{2-} , Cl^- , PO_4^{3-} are easily exchanged with other ions without affecting the structure of the clay mineral [159]. Net negative charge of the mineral generally governs the adsorption efficiency of clays [160].

Bentonite consists of montmorillonite, which has excellent rheological and adsorptive properties is the most commonly utilized clay in water purification [161,162]. It has great affinity toward cationic dyes due to the attraction of opposite charges on the surface of the lattice. Isomorphous substitution results in various types of smectite and causes a net permanent charge balanced by cations in such a manner that water may move between the sheets of the crystal lattice, giving it reversible cation-exchange properties [163]. Other commonly known clays are sepiolite and palygorskite, which are fibrous in nature, having the chemical formulas $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$ and $\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 4\text{H}_2\text{O}$, respectively [164]. Compared with activated carbon clay based adsorbents have good adsorption capacities [165].

1.4 Agricultural Residue Based Adsorbents

1.4.1 Fruit peels

Fruit peels are proved to be excellent adsorbents towards the dyes. Cleaned and grounded mosambi peel powder (180-300 mm) was treated with concentrated sulfuric acid in a weight ratio of 1:1 for 24 hours, followed by washing with NaHCO_3 solution and distilled water and drying. IT showed Erichrome black T dye removal efficiency was 90% at a dye concentration of 50 mg/L and a dsorbent dose of 0.004 g/cc [166]. Higher percentage removal of Mageta MB dye was attained by the use of tapioca peel powder at pH 7 within the contact time of 120 mins [167]. The adsorption capacities decreased in the

order: methyl orange > methylene blue > Rhodamine B > Congo red > methyl violet > amido black 10B for adsorption of dyes from aqueous solutions by using banana and orange peel. The kinetic and equilibrium studies showed better fit of Freundlich equation by banana peel and Langmuir equation for orange peel [168]. Jackfruit peel was used to remove various dyes such as Rhodamine dye with a maximum colour removal of 25.3% at an adsorbent dose of 3.0 g/L and dye concentration of 100 mg/L [169], Methylene blue with the sorption capacity of 285.713 mg g⁻¹ at the optimum pH of 4.0 [170] and the jack fruit peel activated carbon was used as adsorbent in removing Rhodamine –B with the optimal adsorption capacity of 121.47 mg/g, adsorbent dosage (1.2 g/L), and the influence of pH on dye removal was not significant. The maximum color removal percentage achieved was 96% [171]. The jack fruit peel activated carbon was also used as adsorbent in removing a dye, Malachite green, from aqueous solution [172]. Batch mode adsorption experiments are carried out by varying initial dye concentration, temperature and pH and reported that the maximum adsorption capacity attained was 166.37 mg/g at an initial pH of 6.0 and at 32 ±0.5°C. The adsorption capacity of the orange peel adsorbent decreased such as 11.62 mg/g, 10.70 mg/g, 8.61 mg/g, 6.39 mg/g and 5.54 mg/g with increase in temperature in the range of 20°C, 30°C, 40°C, 50°C and 60°C, respectively for Remazol brilliant blue dye from synthetic dye effluent [173]. The maximum monolayer adsorption capacities were found to be 82.64, 123.45 and 142.86 mg g⁻¹ at 303, 313 and 323 K, respectively for the removal of Methylene blue from aqueous solution by Garlic peel [174].

Durian (*Duriozibethinus Murray*) peel was proved to be an effective adsorbent of acid green 25 (AG25) from aqueous solutions at different initial dye concentrations (50-500 mg/L), pH conditions (2-10), and temperature (30-50°C) in a batch mode operation [175]. The results indicated that Durian peel showed good potential for the removal of acid dye from aqueous solution. Broad bean peel was utilized for removal of cationic dye (Methylene blue) and adsorption capacity of 192.7 mg g⁻¹ was found [176]. It was noted that adsorption of dye decreases with an increase in the initial Methylene blue concentration. Activated carbons from fruit peels, namely Citrus documana (NCDC), Citrus medica (NMC) and Citrus aurantifolia (NCAC) showed the adsorption capacity as 0.608 mg/g, 0.580

mg/g and 0.566 mg/g respectively at an initial dye concentration of 20 mg/g and adsorbent dose of 30 g/L for removal of Reactive red 2 dye from effluent [177]. Methylene blue (basic dye) from aqueous solution was removed by Pine apple stem [178] & Pine apple leaf powder [179] at different concentration of dyes, contact time, and pH and maximum adsorption capacity on pine apple stem for the removal of Methylene blue was found to be 119.05 mg g⁻¹ by pine apple stem and The maximum adsorption capacity varied from 0.15 mg/g only by Pine apple leaf powder. Durian peel is potentially useful and attractive adsorbent for removal of Methylene blue from aqueous solution with a flow rate of 15 mL/min showed an early breakthrough time [180].

1.4.2 Grape juice waste as adsorbent

Waste form grape juice was tested to adsorb the Methylene blue dye from aqueous solution and found the highest removal capacity of dye was performed at pH 10 [181].

1.4.3 Sugarcane bagasse

Sugarcane bagasse was treated with various chemical like HCHO, H₂SO₄, ZnCl₂, H₃PO₄, NH₄Cl₂ and NaOH etc., for the adsorption study. As per the study bagasse with particle size between -80 to +230 mesh treated with 1% HCHO in w/v ratio of 1:5 for 4 hours at 50°C and it was activated at 80 °C for 1 day showing higher results compared with the bagasse was treated with sulfuric acid and heated by muffle furnace for 1 day at 150°C, followed by immersing in 1% sodium bicarbonate solution but both these bagasse showed lower adsorption capability when compare with activated carbon [182]. Sugar cane bagasse in untreated, formaldehyde and sulfuric acid treated forms were tested to remove Ethylene red dye from aqueous solution by the above mentioned method [183]. The results showed that H₂SO₄-treated sugarcane bagasse produced higher adsorption when comparing with the HCHO-treated sugarcane bagasse. In an another study one part of 0.05 mm average sized sugarcane bagasse was carbonized without O₂ at 600 °C for 60 minutes. Another part of bagasse powder was immersed in Zinc Chloride Soln. (50% Conc.) and the 3rd part of bagasse powder in phosphoric acid solution (28% Conc.) for 1 day. The investigation found that the removal capability of physically carbonized, ZnCl₂-treated and H₃PO₄-treated bagasse powder was found as 3.48

mg/g, 2.83 mg/g and 1.8 mg/g, respectively [184].

Adsorption experiments were conducted to adsorb reactive dyes such as Remazol Black B dye, Remazol brilliant blue R dye and Remazol brilliant red dye and found that the adsorption capacity was high for Remazol brilliant blue R dye (32.468) followed by Remazol brilliant red dye (18.282 mg/g) and Remazol Black B dye (16.42 mg/g) [185]. Sugarcane bagasse was also tested for removing Methylene blue dye by treating with Conc.H₂SO₄ at 150-160 °C for 1.5 days followed by washing, drying and grinding to 0.33 mm size. The results showed 18% of Methylene blue removal from solution [186]. Adsorption capacity for Basic blue 3 dye and Reactive dye were found as 37.59 mg/g and 34.48 mg/g by untreated and quaternary NH₄Cl₂ (65% w/v) in water treated sugarcane bagasse [187]. Sugarcane dust with the particle size of 351-589 mm was used to adsorb the dyes such as Basic violet 10, Basic violet 1 and Basic green 4 from aq.Soln. and showed the removal capabilities of 50.4 mg/g, 20.6 mg/g and 13.9 mg/g, respectively [188]. Decreasing the flow rate (From 2 L/hr-1L/hr) & the initial concentration of the dye (From 150 mg/L to 100 mg/L), increasing bed height (From 15 cm to 45 cm) & column diameter (From 2.54 cm to 3.50 cm) improved the Orange II dye adsorption by Bagasse ash [189].

Amianted mixture with 10% amine and water at 70°C was produced by treating the sugarcane bagasse, coconut coir pith, cow dung and eucalyptus by 20% NaOH solution followed by protonation by acid, had a better adsorption of 20-26% dye removal for Reactive blue 171, Reactive yellow 84 and Reactive red 141 dyes [190]. The removal efficiency of acid (H₂SO₄)-treated bagasse and the formaldehyde treated bagasse was tested for the adsorption of methyl red dye. It was found the acid treated bagasse showed the better results for removing Methyl red dye over HCHO treated dye [191]; whereas, the formaldehyde-treated bagasse removed more Crystal violet dye over the acid-treated bagasse using the similar treatment method [192].

Adsorption of dye was decreased by increasing its concentration and temperature but, increased with pH and dosage of adsorbent. It was proved by the bagasse in raw and chemically activated forms for the removal of violet dyes. Raw bagasse was found more efficient than the

chemically activated bagasse and the adsorption was decreased by increasing the temperature at the equilibrium time period of 0.5-1 hr [193], since the adsorption rate was first increased and becomes constant by increasing the contact time. It was proved by the equilibrium condition that the buffered solution adsorption at pH 5.8 and 4.5 was quicker than the unbuffered solution for formic lignin from sugar bagasse for the adsorption of Methylene blue at of 40°C and 50°C [194]. The same Methylene blue was adsorbed 18% higher by the chemically activated bagasse than the raw bagasse [195].

1.4.4 Bagasse pith

Residual sugar cane pulp after the extraction of sugar is called as Bagasse pith, which compose huge amount of cellulose, pentosan and lignin [196]. The study was conducted for removal of Astrazone blue, Maxillon red and Telon blue by bagasse pith [197] and proved to be cheaper than the commercially available activated carbon. It was also observed that the bagasse pith removed Remazol Black B, Remazol Brilliant Blue and Remazol Brilliant Red from aqueous solutions by the range of 58–98%, 46–93% and 46-95 %, respectively [198].

1.4.5 Adsorption by rice

Adsorption also influenced by the surface charge of the adsorbent, which is governed by solution pH. By increasing the solution pH, higher cation adsorption was facilitated for the positively charged dyes, namely Malachite green and Methylene blue by rice bran and wheat bran [199]. The effects of particle size, adsorbent concentration and solution ionic strength for the removal was carried out and it was showed that the decreased removal by increasing the concentration of adsorbent, because few adsorption sites retained as unsaturated at the time of adsorption and also by inter-particular interaction.

1.4.6 Husk

The adsorption of Congo red dye from aqueous solution was performed by rice husk carbon by the range of 0.08 g/L activated by steam, showed the adsorption in the range of 10 to 99% at 25 ppm initial dye concentration with the time period of 20 to 200 minutes [205]. The increase in dye adsorption by increasing the contact time was proved by the adsorption of crystal violet was increased from 70% - 82.5% with the time period of 45 minutes. Rice husk carbon, Wheat Straw Carbon and Saw Dust Carbon proved to remove

the orange and magenta by the range of 47% and 77% in ¼ hr at the pH of 6 [199].

1.4.7 Activated rice husk and rice husk ash

Activated rice husk and rice husk ash showed the removal of Methylene Blue in the range of 50 mg/L with the optimum adsorbent dose for RHA was 2.5 mg/L and that for ARH was 20 mg/L at pH 7 with the time period of 40 minutes [200].

1.4.8 Sawdust

Solid waste dust produced by the agricultural activities and forest industries were tested for adsorption, because of their physicochemical properties and cheapest cost. The organic compounds such as lignin, cellulose and hemicelluloses are present with poly phenolic groups which might be helpful in binding dyes by various mechanisms. Saw dust was activated with 240 mL of dioxane, 24 mL of 20% NaOH and 40 ml of epichlorohydrin for 300 minutes at 65 °C followed by filtering, washing and drying and showed Langmuir adsorption capabilities of treated saw dust was higher (188.7 mg/g) over untreated sawdust with 87.7 mg/g [201].

Negatively charged sites are increased and positively charged sites are decreased by increasing the pH. It was proved by Rose wood sawdust for adsorbing Malachite green from aqueous solution and found that initial pH of 6–9 was favorable for dye removal and improved its efficiency by treating with formaldehyde and H₂SO₄ [202]. The adsorption capacity for aqueous solution of reactive dyes such as C.I. Direct Blue 6, C.I. Direct Brown 2, C. I. Direct Green 26, C.I. Direct Brown, C.I. Reactive Red 3, C.I. Basic Blue 86 were tested by Beech wood straw and states that removal of Direct Brown 2 and Direct Brown reduced from 98.6 to 34.7 % and 94.4 to 28.5 %, respectively. The removal capacity of Basic Blue was 97 % at pH 4.4–7 [203]. Acidic dye, Acid yellow was absorbed by Mahogany sawdust and rice husk activated by steam showed the adsorption of 183.3 mg/ g [204]. Diffusion of films controls the adsorption for a shorter duration. It was proved by adsorption of Malachite green by the range of 62.71 mg/g from aqueous solution by Rattan sawdust as adsorbent for the removal of Malachite green from aqueous solution [205].

1.4.9 Cucumis sativa

Cucumis Sativa was studied for the removal of Methylene Blue, Methyl Red and Malachite

Green and found that increase in concentration of adsorbent increased the rate of dye removal and increase in granular size of adsorbent the adsorption decreased at optimum value of pH 6 at 1 hour period [206].

1.4.10 Coir pith

Coir pith was dried, sieved and carbonized at 700 °C and used in the removal of Rhodamine B and Acid violet dyes. Rhodamine B adsorption reached equilibrium stage at 5, 7, 10 and 10 min for dye concentration 10-40 mg/L with increase of 10 mg/L, while for all concentration crystal violet had a equilibrium period of 40 minutes. The removal capacity was determined as 2.56 and 8.06 mg/g of coir pith for Rhodamine B and crystal violet [207]. Coir pith has also proved to remove Procion Orange with the capacity of 2.6 mg/g from waste water Adsorption study was conducted to remove the Coomassie brilliant blue dye by coir pith which was dipped in a HCl solution of one molar concentration, followed by washed with distilled water and dried in an oven at 55 °C as and the results showed that highest removal capacity of 31.84 mg/g [208].

1.5 Micro Organisms

112.5 mm sized Dead cell of brewery yeast was prepared by washing with deionized water followed by drying at 80°C had a removal for Reactive orange 16 dye by the range of 0.604 mg/g, 0.090 mg/g and 0.50 mg/g at pHs of 3, 7 and 10, respectively [209].

1.5.1 *Pseudomonas putida*

Powdered *Pseudomonas putida* was studied for the biosorption of remazol navy blue dye from an aqueous solution and biosorption was estimated to be 20 mg/gm of adsorbent. The equilibrium data satisfied both Langmuir and Freundlich models with freundlich model to fit the data better [210].

1.5.2 *Saccharomyces cerevisiae*

Saccharomyces cerevisiae subsp. *uvarum* cells was modified magnetically and used for the adsorption of Aniline blue, Congo red, crystal violet, Naphthol blue black and Safranin – O from aqueous solutions and the results showed the highest removal amount of the magnetic cells varied considerably for dyes at individual conditions; the maximum adsorption was estimated as 220 mg/g for aniline blue [211]. The dye removal by cassava (*Manihot esculenta*) peel based activated carbon was studied [212].

Cassava peel is an agricultural waste from the food processing industry.

1.5.3 Mango bark and Neem Bark powder

Comparative study was conducted to study the adsorption capacity of Mango bark and Neem bark powder for adsorbing Machelite Green dye. The results indicated that the Langmuir isotherm was well suited than the freundlich isotherm with the value of 0.36 and 0.53 mol/g at 298 K [213]. The adsorption process followed the Pseudo second order model.

1.5.4 Banana stalks

Polyol structure of cellulose-based materials present in banana stalks had a strong physical adsorption of acidic and anionic compounds and chemical adsorption of cations such as metal ions and organic bases [214]. The study was conducted to found out the adsorption of basic dyes with the capacity of 243.90 mg/g.

1.5.5 Ground nut shell

Ground nut shell is generally used for its fuel value. More over its physico-chemical properties, low cost and carbonaceous nature making Groundnut shell as a suitable adsorbent. The adsorption capacity of Ground nut shell powder in order to know the effect on acid dyes removal was studied, by activating with ZnCl₂ solution. The highest removal capacity was estimated to be 55.5 mg/g with the initial adsorbent concentration of 100 ppm [215]. Removal of Malachite green from aqueous solution was also performed by ground nut shell activated by treating it with Zinc chloride. The results showed the adsorption capacity of 94.5% with a dose of 0.5 g/L and initial concentration of 100 mg/L in 30 min equilibrium time, which is slightly lesser than the commercially available activated carbon removal of 96 % of the dye in 15 min [216].

1.6 Removal of Dye Hazelnut

Hazelnut was compared with sawdust of variety of woods for adsorbing Methylene blue and Acid blue. It was found that batch adsorption carried out by ground hazelnut shells had the adsorption of Methylene blue, was up to 1000 mg/L, and Acid Blue 25, up to 500 mg/L in comparison with sawdust. The equilibrium conditions were tested based on the Langmuir's model and maximum removal values towards two dyes were indicated by hazelnut shells than wood sawdust [217].

1.7 Seeds

The cationic adsorption of the papaya seeds was influenced by the initial rate of adsorption. But the process was affected by the intra particle diffusion. The adsorption of Methylene blue by seeds of papaya followed the pseudo-second-order kinetics. Langmuir, Freundlich, and Temkin models were tested for the equilibrium data and it was found that the Langmuir model fitted well with a higher adsorption of 555.557 mg/g [218].

Agricultural solid wastes are available in huge amount with the potential to use as adsorbents because of their physico-chemical characteristics and cheap cost [219]. Sunflower seed hull was tested for the adsorption of Acid violet 17 after activating with H_2SO_4 and the Langmuir adsorption capacity was found to be 116.27 mg/g. The same material also showed the maximum adsorption capacity of 92.59 mg/L at 30°C for the removal of Methyl violet without any physical or chemical treatment [220]. The adsorption was rapid at the outer side of the adsorbent and decreases towards the inner side of the porous. It was proved by the adsorption of Methylene blue from aqueous solution by pumpkin seed hull with a value of 141.92 mg/g at pH 6-9 [221].

1.8 Other Biomasses

1.8.1 Feldspar for dye removal

Feldspar was tested to adsorb dyes from aqueous solutions for the adsorption of three dyes Methylene Blue, Methyl Red and Fluoresceine. Methyl Red and Fluoresceine (acid-base properties) did not show adsorption due to absence of attraction between dyes and adsorbent. Methylene Blue (ox-red properties) showed low adsorption reports to be Pseudo second order chemical reaction kinetics. According to Langmuir isotherm adsorption was estimated as 0.66 mg/g adsorbent at 313 K [222].

1.8.2 Raw and activated prawn shell

Methylene Blue from aqueous solution was adsorbed by prawn shell in raw as well as acid treated form was conducted. Effects of pH, dye and solid concentration and contact time on adsorption were studied. It was found that the Langmuir model fitted better to the adsorption

data compared to the other isotherms studied. It followed a pseudo-second-order kinetic model. The activated form was better than raw prawn waste form with an average difference of 20% in the adsorption of dye. pH 7 and 8 were optimum for activated form and raw form respectively. The raw form and activated form took about 110 minutes and 90 minutes to reach adsorption equilibrium. The amount of maximum dye removal was estimated for initial dye concentration of 25 ppm [223].

1.8.3 Soil

The soil was tested for removal of dyes like Methylene blue, Malachite green and Rhodamine – B, from aqueous solutions [224]. At optimal conditions, the adsorption percentages were found to be 89.18%, 83.20% and 71.56% for Methylene blue, Malachite green and Rhodamine – B, respectively [225-229].

2. CONCLUSION

Among all the methods available for separation of dyes from waste waters, the adsorption shows possible method for treatment and removal of organic pollutants in waste water treatment. This review article presented about different methods available for removal of dyes from various industrial waste water using variety of adsorbents. Adsorption follows surface phenomenon and more advantageous over the other available methods due to its low capital, operation costs and simple design. Adsorption materials are available from various sources such as natural sources, agricultural, and industrial wastes. It is obvious that the adsorption characteristics and structure of adsorbents play a major role in using of them in different places. Characteristics such as adsorption capacity, specific surface area, pore volume, grain size and pore size distribution can effect on removal of contaminations. It is concluded that, the adsorption process is a very effective process for the decolorization of textile wastewater, there is a need to enhance the adsorption process effectively by varying parameters so as to bring down the values to permissible limits for wastewater before discharging it to the water environment.

CONTENT

It is not applicable.

ETHICAL APPROVAL

It is not applicable.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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