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Lignocellulosic Residues for Physical Removal of Harmful Dyes from Industrial Waste Water- Availability, Utilization and Scope

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Abstract : Tonnes of ligno-cellulosic waste are produced worldwide, which is not used any further except, some of it being used for fuel generation and certain other small-scale applications. The need for sustainable methods for preserving the environmental quality that is under immense threat from conventional chemical based industries urgently needs to be investigated and put it into place. Dyes form one of the major industrial pollutants andpossible alternatives to minimize/remove the environmental threat posed by such industrial dye wastewaters in the best economical way possible are seriously required. Reutilization of ligno-cellulosic waste for dye removal from industrial wastewaters offers a feasible, environment friendly and economical solution to this problem. The current review highlights the importance of major ligno-cellulosic waste available worldwide for removal of dyes from industrial wastewaters and reports the worldwide availability of various types of such residues for dye removal, possible mechanisms involved in such applications and future scope of agri-residues for improving the environmental quality.
Key Words : Lignocellulosic waste, Environmental pollution, Industrial dyes.

Introduction

One of the greatest problems we are facing in the current world is that of environmental pollution, which has not only contributed to the deterioration of the human life expectancy and that of animals alike, but the earth itself. The exposure of living systems to different forms of pollutants has led to serious diseases. The increasing industrialization has led to rapid enhancement in concentration of environmental pollutants, causing detrimental changes to the ecosystem. Effluents from various industries produce one form or the other of pollutants, many of which are xenobiotics. The disposal and/or treatment of these highly contaminated effluents is thus of prime importance worldwide and a number of strategies have been tested upon time and again to alleviate the pollution owing to industrial activities. The release of industrial dyes (from industries like, paper, leather and cosmetic industries) into the environment, have posed immense threat to the environment, they are released into. These effluent dyes are thus, one of the major groups of industrial pollutants that are being focused upon by researchers so as to minimize and/or eliminate and save the ecosystem from their ill effects.

Dyes are colored organic compounds having the ability to impart their color unto other objects. They broadly consist of two key components-the chromophores and the auxochromes. The chromophores are responsible for the production of color, and the auxochromes enhances the activities of the chromophore by increasing the affinity of the dye toward the fiber (or material), and also increasing the molecule's overall solubility in water.[1] Dyes are classified into various groups based on several characteristics or features they possess. For instance, dyes are classified based on their solubility, into soluble dyes (includes acid, mordant, metal complex, direct, basic and reactive dyes) and insoluble dyes (includes azoic, sulfur, vat and disperse dyes). Also, the presence of chemically significant structures in dyes is used to classify them. For example, the presence of "azo" group i.e., "-N=N-" or an anthraquinone unit present in some dyes is used to classify dyes into azo dyes or anthraquinone dyes.[1]Dyes are further classified based on the industries commonly using them, such as, textile dyes, paper dyes, cosmetic dyes, etc.[1-3]Furthermore, dyes are categorized as natural or synthetic, depending on how such a dye is obtained or sourced. Though natural and synthetic dyes are extensively used in various industrial applications, yet the synthetic ones are predominantly used for obvious reasons.[4]

It has been established that a significant fraction of these dyes are not completely imparted onto the intended objects resulting in the release of these dyestuffs into the environment as wastewaters fromindustrial wastewaters.[5-9]The release of wastewater containing dyestuff into water bodies and subsequent exposure of aquatic animals to various dyes has been reported to cause death of the animals due to the carcinogenic and toxic nature of these dyes.[9-12]In addition, the photosynthetic activities of aquatic plants especially those in the benthic zone of various water bodies and, planktons, are reportedly affected as these dyes are able to reduce the penetration of sunlight due to their aromatic nature and persistence, thus disrupting the food chain in these water bodies.[4] In human beings, exposure to industrial dyes has been reported to cause allergy, dermatitis, skin irritation and also provoke cancer and mutation.[8]Even very small quantities of these dyes in water bodies is highly toxic and pose a great danger to both aquatic plants and animals, and thus, the removal of these dyes from wastewater of various industries prior to their release into the environment is of the most paramount importance.[12]

In a bid to achieve this, researchers worldwide have investigated various physico-chemical methods. The conventional methods such as, electrocoagulation, adsorption on activated carbon[8], ion exchange, flocculation, froth flotation, ozonation, membrane filtration and reverse osmosis have been studied and applied to remove dyes from wastewater.[1, 8, 9, 13-18]However, a good number of these dyes from industrial effluents by-pass most of these conventional treatment processes and due to their high stability against light, temperature and oxidizing agents, persist in the environment for a long period of time.[9] Generally, most of these existing conventional technologies are often ineffective, expensive and technically complicated. In addition, some of these methods also exhibit high reagent usage, high-energy requirements and the production of toxic secondary pollutants (sludge) in large amounts.[19]Thus, the need to improve on the use of eco-friendly, comparatively cheap methodsof dyeremoval from wastewater is of utmost importance.To this effect, agricultural residues are currently being explored for removal of dyestuffs from industrial wastewaters.[4, 9, 20-22]

Major Agricultural Produce Worldwide and Utilization of Generated Agri-Waste in Treating Dye Wastewaters

Variations in production and utilization of agricultural products in different regions of the world significantly influence the applicability of the lignocellulosic waste for bioremediation. Rice is a staple crop grown on approximately 146 million hectares, which is more than 10 percent of total available land in the world. The total world production of rice was approximately 672,015,587 tons in un-milled or rough rice (paddy) forms as at 2010 and about 738.1 million tonnes as at 2012.[23] It was reported that about 97% of the world's rice is grown by less developed countries, typically in Asia with China and India producing about 55 percent of the total crop.[24] Other countries known to produce rice are Bangladesh, Cambodia, Indonesia, Lao PDR, Myanmar, Thailand and Vietnam, where, rice provides about 56 to 80 percent of the total calories consumed.[25]Reports available in recent years (as of 2012) show China, India, Indonesia and Bangladesh as highest producers of rice with productions values (in metric tons) of 204236000, 157800000, 69056126 and 50497000 respectively [Table 1].[23]In 1993, the major rice exporters were; Thailand (31%), the United States (16%), Vietnam (11%), China (9%), Pakistan (6%), and India (5%)[25] however, recent reports (as of 2012) have seen India becoming the largest exporters of rice followed by Vietnam and Thailand.[26]It is expected that by 2025, more than 5 billion of the world's projected 10 billion people will depend on rice as their principal food. With this in mind, it is predicted that the world will need about 880 million tons of rice in 2025 - 92 percent more rice than was consumed in 1992.[25]

Table 1: Top rice (paddy) producing countries in the world as at 2012.[23]

Rank	Country (Area)	Production (Int. $1000)	Production (MT)
1	China, mainland	50466719	204236000
2	India	40784816	157800000
3	Indonesia	18712225	69056126
4	Bangladesh	8649167	50497000
5	Viet Nam	11680063	43661569
6	Thailand	9430611	37468903
7	Myanmar	7125573	28080000
8	Philippines	4796413	18032422
9	Brazil	3167672	11549881
10	Japan	2939863	10654000
11	Pakistan	2547175	9400000
12	Cambodia	2454554	9290940
13	United States of America	2479417	9051265
14	Republic of Korea	1778686	5934000
15	Egypt	1573564	5911086
16	Nepal	1317015	5072248
17	Nigeria	1309353	4833000
18	Madagascar	906202	4550649
19	Sri Lanka	1041031	3845950
20	Lao People's Democratic Republic	865349	3489210

Rice is usually processed by milling (de-husking and polishing), which often results in the production of certain lignocellulosic wastes in the form of rice husk, rice hull, rice husk/hull ash, rice bran. These are usually of high lignocellulosic contents, and are currently explored as low-cost adsorbents of various pollutants including, several dyes.[27]Several scientific investigations have shown the ability of rice paddy to decolorize various dyes and various regions especially Asian states, can conveniently use it to decolorize industrial wastewaters. These lignocellulosic wastes are preferably used in their native forms due to the high cost of conversion to activated carbon and other treatment techniques.[28] Prominent amongst all lignocellulosic wastes obtained from the cultivation of paddy rice is rice husk. According to the Annual Report of Bernas Sdn Bhd[29], more than 350,000 metric tonnes of rice husks are produced annually as a result of paddy cultivation it is therefore not surprising it has become a favorite amongst investigators. Studies over the last decade, has shown the application of rice husk and other lignocellulosic wastes (obtained from rice) either in their original or pre-treated forms to absorb various dyes. Rice husk in its natural state usually contains high proportions of cellulose [32.34%], hemicellulose [21.34%], lignin [21.44%] and mineral ash [15.05%]. [30,31]The potential use of rice husk to remove two basic dyes; safranine and methylene blue was reported and adsorption capacities of 838mg/g and 312mg/g respectively for each dye were mentioned. [32]Also, rice husk ash, a waste from rice mill, effectively adsorbed acid violet 54, acid violet 49, acid violet 17, acid blue 15 and acid red 119 in aqueous textile solutions with adsorption capacities of this agri-residue for these dyes varying from 99.4 to 155 mg/g. [33]

The effective use of rice husk (activated carbon) to decolorized safranine, methylene blue, ACRY red 4G, malachite green and acid yellow 36, crystal violet, direct orange and magenta dyes have been reported. [34-36,38]Furthermore, utilization of rice husk ash as an adsorbent for methylene blue dye from aqueous solutions was investigated and the highest adsorption capacity was found to be approximately 690 mg/g. [37]The adsorption of indigo carmine using rice husk ash with an adsorption capacity range of 29.3-65.9mg/g has also been reported.[39]EDTA pre-treated rice husk was also used to remove methylene blue and reactive orange dyes and the effects of physical and chemical factors such as, temperature (30^oC-70^oC), concentration of sorbents (0.05g-0.2g) and pH (2-10), agitation (50-200rpm) and particle size were alsoconsidered.[40]Furthermore, reports from this study showed that rice husk in its native state, effectively adsorbed 90.3% and 90.8% of methylene blue in both the single and binary systems, respectively however, the adsorption of reactive orange 16 however, was relatively low. It was also stated that the high affinity of EDTA treated rice husk (ERH) for both MB and RO16 is probably due to the presence of carboxyl and amine groups introduced from the EDTA modification, stating the possibility of the negatively charged carboxyl group to be responsible for the adsorption of positively charged MB whereas the negatively charged RO16 was attracted to the protonated amine group. [40]

Wheat has been the staple food of the major civilizations in Europe, Western Asia, and North Africa for 8,000 years. [41]According to CGIAR Development Dialogues[42], the annual world production of wheat has steadily increased by more than 50% over the past 30 years from 435.7 to 673.7 million metric tons, while the area planted to wheat has decreased slightly from 231.8 to 221.6 million hectares, representative of a substantial increase in yield of over 60%. The report further suggests that some countries however do not produce enough wheat to meet their local demand thus, the need to import from other countries stating that in 2009, the leading importers of wheat in the developing world were Algeria (5.7 million metric tons), Iran (5.5), Brazil (5.4), Indonesia (4.7), Egypt (4.1) and Bangladesh (4.1). It has been reported that a majority of the developing countries involved in the production of wheat are of the Asian continent[40], however, on a global scale, Asian countries only represent approximately 10-15% of known countries involved in wheat production.[43]Report available in recent years depicts China, India, USA and France as highest producers of wheat with production values (in metric tons) of 121023000, 94880000, 61677387 and 40300800 respectively [Table 2]. [43]The world population was projected to be 5.8 billion people at the end of 1997 and is expected to reach 7.9 billion by the year 2025, or approximately, a 35 percent increase.[44]With this in mind, a projection of 786 million tonnes of wheat will be required annually for human use in the year 2025, which represents an annual production increase of 204 million tonnes above production in 1997.[45]During the harvesting and post harvest processing of wheat (especially those carried out by industries involved in wheat flour production), lignocellulosic wastes such as wheat straw and wheat bran are generated and are currently being explored as efficient low cost adsorbents of dyes and other chemical wastes.[27]Wheat straw in its natural state usually contains high proportions of cellulose [30-35%], hemicellulose [26-32%], lignin [16-21%] and mineral ash [4.5-9%].[19,46]

Table 2: Top wheat Producing countries in the world as at 2012.[43]

Rank	Country (Area)	Production (Int. $1000)	Production (MT)
1	China, mainland	14183023	121023000
2	India	14318943	94880000
3	United States of America	8666590	61677387
4	France	5024356	40300800
5	Russian Federation	3063280	37719640
6	Australia	4118269	29905009
7	Canada	3558757	27205200
8	Pakistan	3425066	23473000
9	Germany	1938825	22432000
10	Turkey	2870735	20100000
11	Ukraine	1571918	15762600
12	Iran (Islamic Republic of)	1693316	13800000
13	United Kingdom	1004755	13261000
14	Kazakhstan	984733	9841300
15	Egypt	763010	8795483
16	Poland	689444	8607600
17	Argentina	1207817	8197855
18	Italy	941532	7767300
19	Uzbekistan	573916	6609000
20	Romania	647771	5297748

Over the last decade, several investigators have studied the utilization of wheat-based lignocellulosic waste as low-cost adsorbents of various dyes. The ability of wheat straw to adsorb individual dyes and dye mixtures in solutions was investigated and reported to have achieved 70–75% color removal from 500 ppm dye solutions at room temperature. [47] The removal of dyes (cibacron yellow C-2R, cibacron red C-2G, cibacron blue C-R, remazol black B and remazol red RB) from an aqueous solution by adsorption on three different low cost pretreated (Steam, alkali, ammonia steeping and milling) agricultural residues viz., wheat straw, corncob and barley husk were investigated. A higher percentage of dye removal was achieved at a faster rate by the milled samples proving milling to be a better and more cost effective treatment, except for barley husk which had a higher percentage removal for the control. It was also observed that wheat straw effectively (although slightly lower than the 81% dye removal obtained by1g of pomace) decolorized textile dyes.[48]Furthermore,an adsorption capacity in range of 117.6-196.1mg/g for wheat bran used to absorb reactive blue 19, reactive red 195 and reactive yellow 145 was also reported.[50] Activated wheat husk was also found to absorb reactofix navy blue 2GFN and reactofix golden yellow 3 RFN from an aqueous solution[51, 52] while, wheat straw charcoal was found to effectively adsorb acid violet 17(41%), 49(58%)and 54 (87%) as well as acid blue 15(70%) and acid red 119(22%).[53] The use of wheat straw carbon to successfully remove crystal violet, direct orange and magenta dyes has also been reported.[38]Methylene blue and crystal violet adsorption onto citric acid esterifying wheat straw (EWS) from aqueous solution has also been reported. [54].The use modified wheat straw to adsorb acid red 73 and reactive red 24 from wastewater has also been reported. [55]

Maize (*Zea mays*) also known as Corn in some English speaking countries[57]is the second most produced cereal crop with annual production of 13 billion bushels in the United states alone (as at 2011). [58] Till 2012, maize production was highest in the USA with about 273.8 million tons produced [Table 3]. Other top producers were China, Peoples Rep (205.3), Brazil (71.0), India (22.3), Mexico (22.1), Argentina (21.2) and France (15.6). [58]The lignocellulosic wastes obtained from post-harvesting processing of maize (corn) generated from corn industry including corncob, can be explored for dye absorption from industrial wastewaters. Several reports of use of some of these maize-based lignocellulosics to remove dyes from wastewaters have been made available. For instance, the use of corncobs to decolorize cibacron yellow, cibacron red, remazol black, remazol red, maxilon red, telon blue and erinoyl red have been reported. [49],[59]

Table 3: Top maize producing countries in the world as at 2012.[58]

Rank	Country (Area)	Production (Int. $1000)	Production (MT)
1	United States of America	22233636	273820066
2	China, mainland	10126214	205614000
3	Brazil	2971351	71072810
4	India	2554046	22260000
5	Mexico	1365318	22069254
6	Argentina	2635030	21196637
7	Ukraine	1373511	20961300
8	Indonesia	2012638	19387022
9	France	1336765	15614100
10	Canada	704334	13060100
11	South Africa	1054543	11830000
12	Nigeria	1048014	9410000
13	Russian Federation	273686	8212924
14	Egypt	134814	8093646
15	Philippines	613668	7406830
16	Ethiopia	780289	6158318
17	Romania	415331	5953352
18	United Republic of Tanzania	667938	5104248
19	Germany	62474	4991000
20	Thailand	104322	4947530

Table 4: Top banana producing countries in the world as at 2012.[64]

Rank	Country (Area)	Production (Int. $1000)	Production (MT)
1	India	7004019	24869490
2	China, mainland	2971207	10550000
3	Philippines	2338494	9225998
4	Ecuador	1974865	7012244
5	Brazil	1943868	6902184
6	Indonesia	1743028	6189052
7	Angola	842486	2991454
8	Guatemala	732240	2700000
9	United Republic of Tanzania	711045	2524740
10	Mexico	620675	2203861
11	Costa Rica	541417	2136437
12	Colombia	502420	1982702
13	Thailand	464691	1650000
14	Viet Nam	439344	1560000
15	Cameroon	394283	1400000
16	Kenya	392709	1394412
17	Burundi	333472	1184075
18	Papua New Guinea	299092	1180000
19	Egypt	318180	1129777
20	Dominican Republic	245553	871898

Table 5: Top coconut producing countries in the world as at 2012.[65]

Rank	Country (Area)	Production (Int. $1000)	Production (MT)
1	Indonesia	1990314	19400000
2	Philippines	1731150	15862386
3	India	1167650	10560000
4	Brazil	319393	2931531
5	Sri Lanka	221146	2224500
6	Viet Nam	138216	1272700
7	Papua New Guinea	99515	1210000
8	Thailand	121630	1057000
9	Mexico	116101	1050000
10	Malaysia	67065	606530
11	United Republic of Tanzania	64132	580000
12	Myanmar	47546	421850
13	Solomon Islands	45113	408000
14	Vanuatu	44229	371000
15	Jamaica	34830	315000
16	Ghana	33724	292099
17	Mozambique	29854	270000
18	Nigeria	24326	264814
19	China, mainland	27643	250000
20	Fiji	23220	224380

Table 6: Top pawpaw (papaya) producing countries in the world as at 2012.[66]

Rank	Country (Area)	Production (Int. $1000)	Production (MT)
1	India	1464544	5160390
2	Brazil	430729	1517696
3	Indonesia	257215	906312
4	Dominican Republic	231442	815499
5	Nigeria	219948	775000
6	Mexico	202329	712917
7	Democratic Republic of the Congo	65275	230000
8	China, Taiwan Province of	63004	222000
9	Thailand	61018	215000
10	Guatemala	58605	206500
11	Cuba	50675	178558
12	Philippines	46777	164821
13	Colombia	46526	163939
14	Venezuela (Bolivarian Republic of)	36894	130000
15	Peru	35103	123690
16	Bangladesh	33955	119645
17	Kenya	33461	117903
18	Costa Rica	22704	80000
19	El Salvador	20008	70500
20	Ghana	14190	50000

Table 7: Agri-waste for dye removal

Agricultural waste (adsorbent)	Dyes (adsorbate)	Reference(s)
Rice Husk	Acid blue	33, 80
	Acid red 119	33
	Acid violet 17,49,54	33
	Acid yellow 36	36, 81
	Basic blue 9.	82
	Basic green 4	100, 101
	Brilliant green	103
	Congo red	56
	Crystal violet	101, 104
	Indigo carmine	105, 106
	Malachite green	100, 36, 107, 108
	Methylene blue	32, 37, 40, 109,110,111
	Reactive blue 19	90
	Reactive Orange 16	40
	Reactive red 195	90
	Reactive yellow 145	90
	Safranine Direct red-31 Direct orange-26 Direct orange	32 91 91 91
Rice Straw	Methylene blue	112
Wheat Husk/Bran	Reactive blue 19	50
	Reactive red 195	50
	Reactive yellow 145	50

	Reactofix golden yellow	52
	Reactofix navy blue 2 GFN	51
	Astrazon Black	87
	Astrazon Blue	87
	Astrazon Yellow 7GL	113
	Congo red	114
Wheat Straw	Acid blue 13	53
	Acid red 119	53
	Acid red 73	55
	Acid violet 17,49,54	53
	Reactive red 27	55
	Cibacron Blue	48
	Cibacron Yellow	48
	Cibacron Red	48
	Remazol Black	48
	Remazol Red	48
Banana Peel/Orange Peel	Methyl orange	83
	Methylene blue	83
	Rhodamine B	83
	Congo red	83
	Methyl violet	83
	Amido black 10B	83
	Direct red 23	85
	Direct red 80	85
	Acid violet	85
Peanut Husk	Neutral red	56
Garlic Peel	Methylene blue	95
Date stone	Methylene blue	115
Maize Cob	Astrazon	59
	Maxilon red	59
	Telon blue	59
	Erinoyl red	59
	Cibacron Blue	49
	Cibacron Yellow	49
	Cibacron Red	49
	Remazol Black	49
	Remazol Red	49
Pine Wood	Acid blue 264	86
	Basic blue 69	86
	Basic blue 9	86
Pine Cone	Astrazon Black	87
	Astrazon Blue	87
Cotton Stalk/Hull	Remazol black B	116
	Astrazon black	87
	Astrazon Blue	87

Hazzle Nut Shell	Basic blue 9	99
	Congo red	117
Date Pith	Basic blue 9	118
Coir Pith (waste)	Rhodamine B	88
	Acid violet	88
Coir pith	Congo red	89
Coconut Bunch (waste)	Methylene blue	68, 95
Tea Waste	Methylene blue Janus green Thionine Crystal violet Congo red Neutral red Reactive blue	84,93, 119 84 84 84 84 84 84
Barley Husk	Cibacron Blue	49
	Cibacron Yellow	49
	Cibacron Red	49
	Remazol Black	49
	Remazol Red Solar red BH	49 102
Pawpaw Seed	Methylene blue	94
Sunflower seed hull	Methylene violet	96
Sugarcane Bagasse	Methyl red Methylene blue Gentian violet Crystal violet	120,121 97 97 122
Jute Fiber	Congo red	123
Citrus waste	Reactive blue 19 Reactive blue 49	98 124
Capsicum annuum seed	Reactive blue 49	124
Oreganum stalk	Basic red 18 Methylene blue Acid red 111	92 92 92
Grass waste	Methylene blue	93

Fruits and vegetables waste can be also used as adsorbents of various dyes. *Bananas* and *plantains*, constituting a major source of carbohydrates for millions of people in Africa, the Caribbean, Latin America, Asia and the Pacific, are grown in more than 120 countries, in backyards or in mixed cropping systems by smallholders, and occasionally in monoculture.[60] Major countries known to produce banana and plantain are Burundi, Cameroon, Côte d'Ivoire, Democratic Republic of Congo, Nigeria, Uganda, Rwanda, Tanzania, Colombia, Ecuador, Venezuela, Peru, Bolivia, Asia, Philippines, and Sri-Lanka.[61-63]India, China, Philippines and Ecuador arehigh producers of banana [Table 4].[64]*Coconut* is the most extensively grown nut in the world, the most important palm. It provides people basic needs such as food, drink, shelter, fuel, furniture, medicine, decorative materials and much more.[65] The two biggest producers of coconut are Indonesia (19.4 million ha) and Philippines (15.8 million ha) while India is the third largest producer (10.5 million ha) [Table 5]. In the South Pacific countries Papua New Guinea is the leading producer.[65] In Africa, Tanzania is the largest producer while in Latin America Brazil accounts for more than one half of the total coconut area of that region. Other countries like, A. Asian and Pacific, F.S. Micronesia Fiji, Malaysia, Solomon Islands, Sri Lanka, Thailand, Vanuatu, Vietnam, Western Samoa, Palau, Bangladesh, Myanmar, French Polynesia, Kiribati, Benin, Comoros, Ghana, Ivory Coast, and Madagascar are also known to produce and consume this nut in large quantities.[65]*Pawpaw*(papaya) is an economically important fruit of Caricaceae family. In most producing countries [Table 6], the fruit is consumed as food, or fruit juice.[66]Lignocellulosic wastes from banana, coconut and pawpaw (papaya) have been reportedly used to remove various dyes [Table. 7].

Possible mechanisms for dye removal by lignocellulosic residues

Electrostatic (Columbic) interactions

Dyes are classified as anionic or cationic dyes based on their net charge when dissolved in water. Cationic dyes or basic dyes are dependent on a positive ion; which are generally hydrochloride or zinc chloride complexes. The cationic functionality is found mainly in cationic azo dyes and methane dyes, but also in anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, various polycarbocyclic and solvent dyes.[67] Anionic dyes depend on a negative ion and exhibit characteristic differences in structure such as azoic, anthraquinone, triphenylmethan and nitro dyes. [67]However, a common feature possessed by these dyes, are their water-solubilizing and ionic substituents.[68] The anionic dyes also include direct dyes, which actually includes a large percentage of the reactive dyes.[69] The release of reactive dyes into the environment is undesirable, because they have a low degree of fixation due to the hydrolysis of reactive groups in the water phase.[68] Lignocellulosic compounds on the other hand, have their surface enriched with high cellulosic content and when immersed in water, the cellulosic surfaces becomes partially negatively charged and hence, produce columbic interactions with cationic species of dyes and columbic repulsion with anionic species of dyes in water.[70]

For instance, some researchers[40]attributed methylene blue adsorbing capacity of native rice husk (NRH) to the electrostatic interaction between the partially negative cellulosic surface of the rice husk and the positively charge species (cationic) of methylene blue. They stated that when the dye molecule of MB was placed in water, it dissociated into positively charged species, and as a result, an electrostatic interaction formed between the surface of NRH and MB dye molecule. They further reported that the relatively low uptake of reactive orange 16 by NRH attributing this result to the columbic repulsion between the anionic dye molecules and the negatively charged surface groups of NRH.

Hydrophobic and Hydrophilic Interactions

The balance between the hydrophobic and hydrophilic characteristics of a dye influences its usability in industrial applications.[71] A dye is expected to be hydrophilic enough so as to encourage its solubility in water but should also have a sufficiently strong tendency to come out of solution or suspension and adsorb onto the material that needs to be colored. The hydrophobic nature of chromophoric group of most dyestuff, alternating double and single carbon-carbon bonds and the presence of aromatic groups contributes to hydrophobicity in the dye molecule.[71] Solubility of dyes is achieved by the addition of a suitable number of charged groups such as, sulfonates or amines to the dye molecules, which results in preference of the dye to remain in solution rather than adsorb onto desired material. However, when too little of these suitable charge groups are added to the dye molecule, then the overall solubility of the dye reduces.[71] Lignocellulosic materials are generally hydrophobic in nature. The presence of lignin and cellulose in these materials generally confer a hydrophobic nature. Even though cellulose has three (3) –OH groups in a single pyranose unit it is still not highly hydrophilic.[72] On the contrary, hemicellulose helps to confer hydrophilicity to the lignocellulosic material.[73] Dyes generally have good affinity to the lignin component of the agri-residues.[74-76] Thus, lignocellulosics especially, those with higher lignin content bind to dyes through hydrophobic-hydrophilic interactions. Labek and Wardas[77] further accredited the higher adsorption tendency of cationic dyes to interaction with the presence of the negatively charged sites on the lignin.

Physical entrapment

Physical entrapment usually occurs with neutral dyes such as Vat, Sulfur and Napthol dyes. These dyes are usually insoluble and thus are easily entrapped physically in the pores of the lignocellulosic. The surface area of the lignocellulosic material and the pore size distribution on the material are key factors that determine the amount of dye that is absorbed by the lignocellulosic material. The surface area doesn't necessarily refer to the external surface of the lignocellulosic material only but also inclusive of the internal surface area. In fact, lignocellulosic materials have been shown with lesser external surface area but larger internal surface area to adsorb various dyes. The contact time between the material and dye solution is found to be a crucial factor that influences the success of dye absorption. Essentially, the longer the contact time the more of the dye adsorbed.[71] Furthermore, depending on the length of the contact time, even relatively large molecules are found to permeate deep within the cell wall of wood fibers.[78, 79]

Others

Formation of hydrogen bonds usually seen in negatively charged, soluble dyes such as direct dyes and covalent bonds usually observed in negatively charged, soluble dyes such as, Reactive dyes has also been reported.[71]

4. Scope of agri-residues forindustrialdye removal

Future projections for the requirements of various agricultural products such as rice, wheat and maize are very high. For instance, it is expected that by 2025, more than 5 billion of the world's projected 10 billion people will depend on rice as their principal food. With this in mind, it is predicted that the world will need about 880 million tons of rice in 2025 - 92 percent more rice than was consumed in 1992.[25] Also, assuming little or no change in world per caput consumption of wheat, a projection of 786 million tonnes of wheat will be required annually for human use in the year 2025, an annual production increase of 204 million tonnes above production in 1997.[45] This invariable means the increased availability of various lignocellulosic wastes resulting from the processing of these agricultural products for use as physical adsorbents of dyestuff from industrial wastewaters and from the various investigations conducted by researchers over the last decade or more, it has become evident from their reports that these lignocellulosic waste can indeed effectively serve as a low-cost alternative to dye-removal (from) wastewater. Conventional techniques such as electrocoagulation, adsorption on activated carbon, ion exchange, flocculation, froth flotation, ozonation, membrane filtration and reverse osmosis, which are in comparison to the use of lignocellulosic wastes, more expensive and produce toxic intermediates.

Although, more investigations needs to be done using other lignocellulosic wastes (especially those poorly investigated) so as to develop and improve already existing techniques, current information and data indicates great progress with regards to the feasibility of utilizing these lignocellulosic wastes as physical adsorbents of dyes from industrial waste wasters.

5. Conclusion

Rapidly changing environmental conditions in response to ferocious addition of harmful pollutants to the ecosystem has rung the alarm bell for scientists, industrialists, environmentalists as well as the highly aware public, all over the world for desperate measures to alleviate the environmental pollution in the best possible way. The eminence of any process selected has to be carefully and delicately balanced with the environment and economic concerns for a sustainable solution to the dye problem worldwide.Tonnes of Lignocellulosic wastes, that is simply disposed off in the environment proposes to be a powerful solution to the given problem. Further studies need to highlight the integration of agricultural industrial sectors with dye-based industries for exploring the waste generated by the former as a boon for the latter.

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