STUDY OF REMOVAL TECHNIQUES FOR DYES BY ADSORPTION: A REVIEW

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ABSTRACT

Various dyes present in water have adverse effect on human life, plants and on animals. There are various technologies used to effectively remove these dyes from effluent water. The methodology, advantages and disadvantages of various technologies are discussed in detail. Adsorption of dyes, the matter of this review, is a resourceful, low-cost and environmentally caring remedy for a host of pollutants. These may be of biological, organic and inorganic in origin within water. The efficient and successful application of adsorption demands that the pollutant, source of adsorbent are in close proximity or contact with each other. The ability of adsorption technology to remove low levels of persistent organic pollutants as well as microorganisms in water has been widely demonstrated and, progressively, the technology is now being commercialized in many areas of the world including developing nations. This review considers recent developments in the research and application of adsorption for the treatment of dyes in water. The review considers transport characteristics on the adsorbent surface, reactor design and organic degradation. The effects of adsorption operating parameters on the process are discussed in addition.

Keywords: Dye removal, Adsorption, Biological, Chemical

1. INTRODUCTION

Various treatment methods are available for the removal of dyes from the wastewater. Many chemical, physical and biological methods are generally used to remove dyes from the industrial effluent. Various chemical methods are oxidative processes, H_2O_2 -Fe (II) salts (Fenton's reagent), and ozonation, photochemical, sodium hypo chloride (NaOCl), cucurbituril and electrochemical destruction. Physical treatment methods for the removal of dyes are adsorption, membrane filtration, ion exchange, irradiation and electro kinetic coagulation. The critical literature review of all these methods is discussed in this paper.

1.1 Treatment Methods of Dyes

1.1.1 Chemical methods:

1.1.1.1 Oxidative processes:

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This is the most commonly used method of decolonization by chemical means. This is mainly due to its simplicity of application. The main oxidizing agent is usually hydrogen peroxide (H_2O_2) [Rosario et al., 2002]. This agent needs to be activated by some means, for example ultra violet light. The methods of chemical decolonization vary by the way in which the H_2O_2 is activated [Slokar and Marechal, 1997].Chemical oxidation removes the dye from the dye-containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules [Raghavacharya, 1997].

1.1.1.2 H₂O₂-Fe (II) salts (Fentons reagent):

Fentons reagent is a suitable chemical means of treating wastewaters which are resistant to biological treatment or is poisonous to live biomass [Slokar and LeMarechal, 1997]. Chemical separation uses the action of sorption or bonding to remove dissolved dyes from wastewater and has been shown to be effective in decolorizing both soluble and insoluble dyes. One major disadvantage of this method is sludge generation through the flocculation of the reagent and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. It has conventionally been incinerated to produce power, but such disposal is seen by some to be far from environmentally friendly. The performance depends on the final floc formation and its settling quality, although cationic dyes do not coagulate at all. Acid, direct, vat, mordant and reactive dyes usually coagulate, but the resulting floc is of poor quality and does not settle well, yielding mediocre results [Raghavacharya, 1997].

1.1.1.3 Ozonation:

The use of ozone was pioneered in the early 1970s, and it is a very good oxidizing agent due to its high instability (oxidation potential, 2.07) compared to chlorine, another oxidizing agent (1.36), and H_2O_2 (1.78). Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons [Lin and Lin, 1993]. The dosage applied to the dye-containing effluent is dependent on the total color and residual COD to be removed with no residue or sludge formation and no toxic metabolites [Gahr et al., 1994]. Ozonation leaves the effluent with no color and low COD suitable for discharge into environmental waterways. This method shows a preference for double-bonded dye molecules [Slokarand Marechal, 1997]. One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. A disadvantage of ozonation is its short half-life, typically being 20 min. This time can be further shortened if dyes are present, with stability being affected by the presence of salts, pH and temperature.

1.1.1.4 Photochemical:

This method degrades dye molecules to CO_2 and H_2O [Zamora et al., 1999] by UV treatment in the presence of H_2O_2 . Degradation is caused by the production of high concentrations of hydroxyl radicals. UV light may be used to activate chemicals, such as H_2O_2 , and the rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition [Slokar and Marechal,1997; Rosario et al., 2002]. This may be set-up in a batch or continuous column unit [Namboodri and Walsh, 1996]. Depending on initial materials and the extent of the decolonization treatment, additional by-products, such as, halides, metals, inorganic acids, organic aldehydes and organic acids may be produced. There are advantages of photochemical treatment of dye containing effluent like no sludge is produced and foul odors are greatly reduced. UV light activates the destruction of H_2O_2 into two hydroxyl radicals.

1.1.1.5 Sodium hypochlorite (NaOCl):

This method attacks at the amino group of the dye molecule by the Cl^+ . It initiates and accelerates azo bond cleavage. This method is not suitable for dispersed dyes. An increase in decolonization is seen with an increase in Cl concentration. The use of Cl for dye removal is becoming less frequent due to the negative effects, it has when released into waterways [Slokar and Marechal, 1997] and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules [Banat et al.,1999].

1.1.1.6 Cucurbituril:

Cucurbituril was first mentioned by Behrand et al. [1905], and thenre discovered in the 1980s. It is a cyclic polymer of glycoluril and formaldehyde [Karcher et al., 1999a, b]. Cucurbituril named, because its structure is shaped like a pumpkin (member of the plant family *Cucurbitaceous*). The uril indicates that an urea monomer is also part of this compound. Buchman [1992] showed extra ordinarily good sorption capacity of cucurbituril for various types of textile dyes. Cucurbituril is known to form host-guest complexes with aromatic compounds and this may be the mechanism for reactive dye adsorption. Another proposed mechanism is based on hydrophobic interactions or the formation of insoluble cucurbituril dye-cation aggregates since adsorption occurs reasonably fast. To be industrially feasible, Cucurbituril would need to be incorporated into fixed bed sorption filters [Karcher etal., 1999b]. The cost of its application is a major disadvantage of this method.

1.1.1.7 Electrochemical destruction:

This is a relatively new technique, which was developed in the mid 1990s. It has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up.

Electro chemical methods have been successfully applied in the purification of several industrial wastewaters as well as landfill leachate [Vlyssides et al. 1999]. The breaks down metabolites are generally not hazardous leaving it safe for treated wastewaters to be released back into water ways. It shows efficient and economical removal of dyes and a high efficiency for color removal and degradation of recalcitrant pollutants [Ogutveren and Kaparal, 1994; Pelegrini et al., 1999]. Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals.

1.1.2 Physical treatments:

1.1.2.1 Adsorption:

Adsorption produces a high quality product, and is a process which is economically feasible [Choy et al., 1999]. Almost complete removal of impurities with negligible side effects explains its wide application in tertiary treatment stages and polishing stages. Many researchers have studied the feasibility of using low cost materials, such as saw dust (SD) Naiya et al., 2009; Garg et al., 2003; Kalavathy and Miranda, 2010; Sharma et al., 2009; Ahmad et al., 2009], waste orange peel[Namasivayam et al., 1996], bagasse fly ash [Mane et al., 2007a], rice husk ash [Maneet al., 2007b], banana pith [Namasivayam et al., 1998], bottom ash [Gupta et al., 2004; Gupta et al., 2009; Mittal et al., 2005], deoiled soya [Mittal et al., 2008], rice husk [McKay et al., 1986] and kaolin [Nandi et al., 2009]. The other researchers also utilized adsorbents such as bentonite clay [Ramakrishna and Viaraghavan, 1997], neem leaf powder [Bhattacharya and Sharma, 2003 and Bhattacharya and Sharma, 2005], powdered activated sludge [Kargi and Ozmihc, 2004], perlite [Dogan and Alkan, 2004], powdered peanut hull [Gong et al., 2005], Natural and modified clays like sepiolite [Mahir et al., 2005], zeolite [Armagan et al., 2004], bamboo dust[Kannan and Sundaram, 2001] as low cost adsorbents. Other low cost adsorbents like coconut shell [Manju et al., 1998], groundnut shell [Kannan and Sundaram, 2001], rice straw [Hameed and El-Khaiary, 2008], duck weed [Waranusantigul et al., 2003], sewage sludge [Otero et al., 2003], sawdust carbon [Jadhay and Vanjara, 2004], agricultural waste and timber industry waste carbons [Bansal et al., 2009] and gram husk [Jain and Sikarwar, 2006] have used for removal of various dyes from wastewaters. Critical review of low cost adsorbents for wastewater treatment has been presented by earlier researchers [Gupta and Suhas, 2009; Mall et al., 1996; Bailey etal., 1999; Demirbas, 2009]. The table 2.1 gives the summary of the literature review for removal of BG, CR and other dyes by adsorption technique.

1.1.2.2 Membrane filtration:

This method has the ability to clarify, concentrate and most importantly, to separate dye continuously from effluent [Mishra and Tripathy, 1993]. It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment, and microbial attack. The concentrated residue left after separation poses disposal problems and high capital cost and the possibility of clogging, and membrane replacement is its disadvantages. This method of filtration is suitable for water recycling within a textile dye plant if the effluent contains low concentration of dyes, but it is unable to reduce the dissolved solid content, which makes water re-use a difficult task.

1.1.2.3 Ion exchange:

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes [Slokar and Marechal, 1997]. Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. A major disadvantage of this method is cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dyes [Mishra and Tripathy, 1993].

1.1.2.4 Irradiation:

Sufficient quantity of dissolved oxygen is required to break down the organic substances effectively by radiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. This has an effect on cost. Dye containing effluent may be treated in a dual-tube bubbling reactor. This method showed that some dyes and phenolic molecules can be oxidized effectively at a laboratory scale only [Hosono et al., 1993]. In this study, the possibility of using gamma rays to degrade or decolorize reactive dyes in water was investigated [Dilekand Olgun, 2002].

1.1.2.5 Electro coagulation:

Electro coagulation method utilizes direct current to produce sacrificial electrode ions, which removes undesirable contaminants either by chemical reactions and precipitation or by causing colloidal materials to coalesce and then be removed by electrolytic floatation. Electro coagulated sludge contains less bound water besides being more shear

resistant and readily filterable. The table 2.1 gives the summary of the literature review for removal of BG, CR and other dyes by electro coagulation technique.

1.1.2.6 Coagulation flocculation:

It is one of the most popular conventional treatment methods. Polyelectrolytes are widely used coagulant aids as cationic, anionic and non anionic additives. The sludge produced by polyelectrolyte is usually compact and easy to dewater for subsequent treatment and disposal. It involves the addition of ferrous sulphate and ferric chloride, allowing excellent removal of direct dyes from wastewaters. The optimum coagulant concentration is dependent on the static charge of the dye in solute on and difficulty in removing the sludge formed as part of the coagulation is a problem [Mishra and Tripathy, 1993]. Production of large amounts of sludge occurs, and this results in high disposal costs [Gahr et al., 1994]. The table 2.1 gives the summary of the literature review for removal of BG, CR and other dyes by coagulation/flocculation technique.

1.1.3 Biological treatments:

1.1.3.1 Decolonization by white-rot fungi:

White-rot fungi are able to degrade dyes using enzymes, such as lignin peroxides (LiP) or Manganese dependent peroxidases (M_nP). Other enzymes used for this purpose include H_2O_2 -producing enzymes, such as, glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenoloxidase enzyme [Kirby, 1999]. These are the same enzymes used for the lignin degradation. Azo dyes, the largest class of commercially produced dyes, are not readily degraded by micro-organisms but these can be degraded by *P. chrysosporium*. Other fungi such as, *Hirschioporuslarincinus, Inonotushispidus, Phlebiatremellosa and Coriolusversi color* have also been shown to decolorize dye-containing effluent [Banat et al., 1996; Kirby, 1999].

1.1.3.2 Other microbial cultures:

Mixed bacterial cultures from a wide variety of habitats have also been shown to decolorize the diazo linked chromospheres of dye molecules in 15 days [Knapp and Newby, 1995]. Nigam and Marchant [1995] and Nigam et al., [1996] demonstrated that a mixture of dyes were decolorized by anaerobic bacteria in 24-30 h, using free growing cells or in the form of bio films on various support materials. Ogawa and Yatome [1990] also demonstrated the use of bacteria for azo dye bio degradation. These microbial systems have the drawback of requiring a fermentation process, and are therefore unable to cope with larger volumes of textile effluents. Yeasts, such as *Klyveromycesmarxianus*, are capable of decolorizing dyes. Banat et al., [1997] showed that *K. marxianus* was capable of decolorizing Remazol Black B by 78-98%.Zissi et al., [1997] showed that *Bacillus subtilis* could be used to break down p-aminoazo benzene, a specific azo dye. Further research using mesophilic and thermophilicmicrobes have also shown them to degrade and decolorize dyes [Nigam et al., 1996; Banat et al., 1997].

1.1.3.3 Adsorption by living/dead microbial biomass:

The uptake or accumulation of chemicals by microbial mass has been termed Biosorption [Hu, 1996; Tsezos and Bell, 1989]. Dead bacteria, yeast and fungi have all been used for the purpose of decolorizing dye-containing effluents. The use of biomass has its advantages, especially if the dye-containing effluent is very toxic. Biomass adsorption is effective when conditions are not always favorable for the growth and maintenance of the microbial population [Modak and Natarajan, 1995]. Adsorption by biomass occurs by ion exchange. Biosorption tends to occur reasonably quickly: a few minutes in algae to a few hours in bacteria [Hu, 1996]. This is likely to be due to an increase in surface area caused by cell rupture during autoclaving [Polman and Brekenridge, 1996].

1.1.3.4 Anaerobic textile-dye bioremediation systems:

Azo dyes make up 60-70% of all textile dyestuffs [Carliell et al., 1995]. Azo dyes are soluble in solution, and are not removed via conventional biological treatments. Reactive dyes have been identified as the most problematic compounds in textile dye effluents [Carliell et al., 1996, 1994]. A major advantage of this anaerobic system, apart from the decolonization of soluble dyes, is the production of biogas. Biogas can be reused to provide heat and power, and will reduce energy costs.

1.1.4 Studies on removal of Dyes using various treatment methods:

The table 1.1 gives the summary of the literature review for removal of BG, CR and other dyes by adsorption, electro coagulation, electrochemical and coagulation/flocculation techniques.

References	Process/Adsorbent	Adsorbate/other	Operating	Results and discussion
Makayat	Sorbail ailian	A stra zona blua	Patah	Equilibrium time increases with increase in
MCKay et	Solosii sinca	Astrazone blue	Daten	Equilibrium time increases with increase in
al.,				concentration. Adsorption increases with
1980a				decrease in particle size. The rate-
				controlling step is mainly intra particle
				diffusion. Adsorption increased with
				increase in temp. However adsorption
				capacity decreased with increase in time.
Mckay et al.,	Silica	Astra zone blue	Batch,	Results indicate that silica has the ability to
1980b		(Basic blue 69)	Fixed	remove considerable quantities of Astra
		di seconda d	and	zone blue dye, BDST model is
		all is a second second	Fluidized	inapplicable, C ₀ =200 mg/l, pH=5.1.
Mckay et al.,	Silica	Astra zone blue	Batch,	Results indicate that silica has the ability to
1980b		(Basic blue 69)	Fixed	remove considerable quantities of Astra
		5	and	zone blue dye, BDST model is
			Fluidized	inapplicable, C ₀ =200 mg/l, pH=5.1.
		100		
Mckay et al.,	Wood	Astra zone blue	Batch	Adsorption of telon blue increased whereas
1980c	ATA	and Telon blue	- /	of astra zone blue decreased with rise of
				solution temperature. Wood particle size
	1 Y 1			=150-25 μm.
McKay et	Peat	Astra zone blue	Batch	Adsorption increases with temp. Increase,
al.,	10.7 JU		1 11	film diffusion to be the rate-controlling
1981	88 E	1 1		step.
McKay et	Wood bark, rice	Sandolan,	Batch	None of the adsorbents adsorbed sandolan
al.,	husk, coal,	Rhodamine,		blue or sandolan Rhoda mine, Bentonite
1986	bentonite	Safranine, Congo	1.0	was best overall, followed by tree bark.
1	clay, hair and	Foron Bril red.		cotton waste and rice husk. $C_0=50-1000$
	cotton waste	Methylene blue.		mg.
	No. W	Solar blue, Foron	100	6
	1 A.	blue		V /35
Gupta et al	Coal (Singrauli)	Chrome dye	Batch	100% at $C_0=5$ and 80.77% at $C_0=20$ mg/l.
1987	53 um	(Met omega		The decrease in removal 97.66 to 71.09
	55 pill	chrome orange)		with rise in temp 30 to 50° C C ₀ =5-20
		enionia orange)		$mg/1$. Temp=30 to $50^{\circ}C$
Gupta et al.	Fly ash	Chrome dye	Batch	Higher removal at low pH concentration
1988a	11) 4011	(Metomega	Duron	and particle size. Rate controlling step is
		chrome orange)		mainly intra particle diffusion $C_0=5-20$
	1	entonie orange)		mg/1, pH=3.0-11.8. Particle size=53-300
			C-STATE CONTRACTOR	
Gunta et	Fly ash	Omega chrome	Batch	98.85% removal of dye in the acidic range
al 1988b	TTy ash	red dye	Daten	$pH-4.2$ T = $30^{\circ}C$ Dose = 1.0 g Volume
al.,19000		icu uye		50ml
Gunta at al	China alay	Chroma dua	Patch	First order reaction diffusion controlled
10880	China Clay	Rotch	Daten	First order reaction, diffusion controlled.
Mall at al	Fly ash Pottom ash	Methylana blua	Batch	Higher eathon contant bottom ash proved
1004	Thy ash bottom ash	Mothylelle blue,	Daten	more nouverful adaptions there for 1
1994		Nietnyi Violet,		nore poweriul adsorbent than ily ash.
		Dhodomino D		Contact time of 20.45 min and all 9 and
		A sid and S		Contact time of $50-45$ min. and pH 8 and
		Acia orange, Sun		5.0
		last yellow,		
	1	Malachite green	1	

Table1.1Studies on removal of Dyes using various treatment methods

Mall et al., 1995	Bottom ash	Methylene blue, Malachite Green	Batch and Column	Removal to the extent of 95 to 100 percent in low concentration ranges and increase in agitation gives higher removal.
Liversidge et al.,1997	Linseed cake	Basic Blue 41	Batch	The Langmuir equation described the adsorption well. The enthalpy of adsorption was found to be endothermic and the capacity of the linseed cake for the dye decreased with increasing temperature. The linseed cake was compared with peat and it was found that it had a greater capacity for the dyestuff than peat.
Khattri et al., 1998	Mixture of alumina and clay (1:2)	Methylene blue, Malachite green, Crystal violet, Rhodamine B	Batch	Maximum removal occurs in initial 35-40 min. With increase in initial concentration from 6 -12 mg/l of dye, the % removal decreased. Optimum pH 7.2 and temperature 25^{0} C. Batch: 2.0g adsorbent, 200 ml aqueous solution of dye, shaking 200 rpm.
Khattri et al., 1999	Sagaun sawdust	Methylene blue, Malachite green, crystal violet, Rhodamine B	Batch	Maximum removal for Methylene blue 86%, Malachite green 83%, Rhodamine B 58%, Crystal violet 89%. At concentration 6 mg/1, pH 7.5, and 30° C, 0.5 g/200ml dose was used.
Vlyssides et al., 1999	Electrochemical Technique	Textile dye wastewater	Batch	Textile dye wastewater TDW from a reactive azo dyeing process was treated by an electrochemical oxidation method using Ti/Pt as anode and stainless steel 304 as cathode. These results indicate that this electrolytic method could be used for effective TDW oxidation or as a feasible detoxification and color removal pretreatment stage for biological post treatment.
Boon et al., 1999	Coagulation/ flocculation technique	Textile wastewater	Batch	The effective range of pH for the MgCl ₂ treatment is between 10.5 and 11.0, and beyond the range, the percentage of color removal decreases tremendously. Flocs formed by the MgCl ₂ treatment are found to give shorter settling time than the alum and PAC treatment. The MgCl ₂ treatment has been used on the industrial dye waste, the removal rates of 97.9% for coloring matter, 88.4% in COD and 95.5% suspended solid can be achieved. Polyelectrolyte, Koaret PA is commonly used as a coagulant aid to improve the coagulation process and subsequently the floc settling velocity.
Chun and Wang, 1999	Decolonization and biodegradability of photo catalytic treated azo dyes	Reactive Yellow KD-3G-, Reactive red 15, Reactive red 24	Batch	Greater than 90% of color removal of most dyes solution was achieved after 20-30 min. treatment. COD and TOC in wastewater were also reduced from 60% to 85%. It was found that BOD in wastewater was increased after photo oxidation. This indicates that the biodegradability of the wastewater can be enhanced by photo

				catalytic oxidation. The BOD/COD of wastewater was generally more than 0.30 when their color disappeared completely. The result implies that the optimal exposing time to photocalatysis process is the period for complete decolonization. The photo catalysis process could be an alternative for decolonization and further color removal of dyes from wastewater as pre-or post -treatment of conventional biological process.
Buning Chen et al., 2001	Bagassepith	Acid Blue 25 (AB25), Acid Red 114 (AR114), Basic Blue 69 (BB69) and Basic Red 22	Batch	C_0 =50-150mg/l. The equilibrium isotherms of four adsorption systems of dyestuffs (AB25, AR114, BB69 and BR22) on pith can be formulated precisely by the Langmuir equation. There are different minimum values of the contact time for the optimizations of a two-stage batch adsorber system at different process conditions. There is a significant difference among these optimal results (minimum contact time changes from 751 to 533 min for the AB25-pith system, 959 to 672 min for the BR22-pith system).
Dilek and Olgun, 2002	By gamma irradiation	Reactive Blue 15 and Reactive Black 5	Batch	In this study, the possibility of using gamma rays to degrade or decolorize reactive dyes in water was investigated. Two different reactive dyes (Reactive Blue 15 and Reactive Black 5) in aqueous solutions were irradiated at doses of 0.1–15 kGy, at 2.87 and 0.14 kGy/h dose rates. The COD reduction for all the dye solutions was approximately 76–80% at 1 and 15 kGyfor RB5 and RB15.
Ghoreishi and Haghighi, 2003	Chemical catalytic reaction and biological oxidation	Direct, Basic and Reactive colors	Batch	The optimum dosage for treatment of actual wastewater was found to be 50–60 mg/l for catalyst bisulfate and 200–250 mg/l for sodium boro hydride. Finally, a bench-scale experimental comparison of this technique with other reported combined chemical-biological methods showed higher efficiency and lower cost for the new technique. The results of this study indicate that a combined reduction- biological treatment method is a viable technique to effectively decrease the color, BOD, COD and TSS by 74–88%, 97–100, 76–83 and 92–97%, respectively.
Georgiou et al., 2003	Coagulation/ flocculation techniques	Textile wastewater	Batch	Lime (Ca(OH) ₂) and ferrous sulfate (FeSO ₄ 7H ₂ O) of commercial grade were utilized for the experimental procedure. Treatment with lime alone proved to be very effective in removing the color (70–90%) and part of the COD (50–60%) from the textile wastewater. Finally, the treatment with lime in the presence of

				increasing doses of ferrous sulfate was tested successfully, however; it proved to be very costly mainly due to the massive production of solids that precipitated.
Sun et al., 2003	Adsorption on modified peat-resin particle	Basic Magenta and Basic Brilliant Green	Batch	$C_0=100-400$ mg/l, Agitation speed=200- 500 rpm, particle size=0.8-5 mm, The adsorption isotherm showed that the adsorption of basic dyes on modified peat- resin particle deviated from the Langmuir and Freundlich equations. The pseudo-first order, pseudo-second order and intraparticle diffusion models were used to fit the experimental data. The change of agitation speed did not cause significant difference of intraparticle diffusion
Krishna et al., 2003	Adsorption on Neem leaf powder	Brilliant Green	Batch	parameter in experimental conditions. A novel adsorbent was developed from mature leaves of natural Neem trees for removing dyes from water. The pH of the aqueous solutions of Brilliant Green was 6.5 which did not change much with dilution. The dye solution is pH-sensitive, it becomes turbid if the pH is lowered and it changes color if the pH is increased. Therefore, all the adsorption experiments were done without adjusting the pH. The adsorption experiments were conducted in the concentration range of 2.07*10-2 to 10.36*10-2mmol/m ³ at four different temperatures of 300, 303, 313 and 323 K with adsorbent dose of 0.13–0.63 g/m ³ . If the adsorbent dose was increased to 0.63 g/m ³ , the removal of the dye further increased to 98%. The adsorption of the dye, Brilliant Green, was found to be endothermic indicating that the adsorption would be enhanced if the temperature of adsorption was a little above the ambient temperature. However, adsorption at ambient temperature was also substantial. The values of the adsorption coefficients, calculated from Langmuir and Freundlich equations agree well with the conditions of favorable adsorption
Gulnaz et al., 2004	Activated sludge	Basic Red 18 and Basic Blue 9	Batch	The activated sludge had the highest dye uptake capacity, having the monolayer adsorption capacity 285.71 and 256.41 mg/g for Basic Red 18 and Basic Blue 9, respectively, at pH value of 7.0 and 20 ⁰ C. The equilibrium data fixed very well with
Garg et al., 2004	Adsorbents prepared from Prosopis Cineraria sawdust—an agro- industry waste	Malachite green	Batch	both the Langmuir and Freundlich models. The adsorbents included formaldehyde- treated sawdust (PCSD) and sulphuric acid- treated sawdust (PCSDC). Similar experiments were carried out with commercially available coconut based

				carbon (GAC) to evaluate the performance of PCSD and PCSDC. Adsorption efficiency of different adsorbents was in the order GAC>PCSDC>PCSD. An initial pH of the solution in the range 6–10 was favorable for the malachite green removal for both the adsorbents. These experimental studies have indicated that PCSD and PCSDC could be employed as low-cost alternatives in wastewater treatment for the removal of dyes. Fixed adsorbent dose (0.4g/100 ml), natural pH and at different initial concentrations of malachite green (50, 100, 150, 200 and 250 mg/l) for different time intervals up to equilibrium time (3h).
Xiang et al., 2005	By reaction with potassium permanganate	Reactive , Direct and Cationic dyes	Batch	Decolonization of dye solutions by potassium permanganate was studied. When pH value <1.5, the decolonization efficiency was very high. When pH value >4.0, the dye solutions were almost not decolorized by potassium permanganate. Concentration of potassium permanganate and temperature had significant effects on the decolonization efficiency. The results of the treatment of real wastewater by potassium permanganate indicated that oxidation of textile wastewater by potassiumpermanganate might be used as a pre-treatment process prior to biological treatment.
Chakraborty et al., 2005	Adsorption and nano filtration	Reactive red CNN and reactive black B	Batch	A combination of adsorption and nano filtration (NF) was adopted for the treatment of a textile dye house effluent containing a mixture of two reactive dyes. The effluent stream was first treated in a batch adsorption process with sawdust as an adsorbent to reduce the dye concentration of the effluent by about 83% for Dye 1 and 93% for dye 2. The effluent from the adsorption unit was passed through an NF unit for the removal of the remaining small amount of dyes and to recover the associated chemicals (mainly salt) in the effluent stream. The dyes remaining after this step were less than 1 ppm.
Chakraborty et al., 2005	The adsorbent is prepared from hard wood saw dust	Crystal violet	Batch	It is seen that about 341mg of crystal violet can be removed using 1g of the adsorbent at 298K. Particle size of the adsorbent (0.04–0.23mm), initial concentration of the dye (75–200mg/1), temperature (288– 323K) and the amount of adsorbent (0.5– 2.0 g). All experimental runs are taken using a high stirrer speed (2500rpm) and neutral pH. Adsorption increases with

				decrease in particle size, increase in
				temperature at lower temperature.
Hosny et al.,	By reaction with	Direct Green 28	Batch	It is used in the current work to oxidize and
2005	hydrogen peroxide	and Direct		decolorize two of the direct dyes that fulfill
		Blue 78		an outstanding demand. The oxidation
				reaction of I showed a first order kinetics
				for $[H_2O_2]$ and zero-order kinetics for
				[Dye]. The oxidation reaction of II showed
				a first order kinetics for both [dye] and [Cu
				(II)] and zero-order kinetics for $[H_2O_2]$
Garget al.,	Indian Rosewood	Basic dye	Batch	Optimum pH=7. Higher adsorption
2005	sawdust: a timber	(Methylene blue)		percentages were observed at lower
	industry waste	ALC: NOT THE OWNER	and the second second	concentrations of methylene blue.
		the second second second		Experiments were conducted with GAC,
				SDC (Sulphuric acid treated sawdust
	100 million -	1		(SDC)) and SD (Formaldehyde treated
		1		sawdust)at constant adsorbent dosage (0.4
				g/100 ml), pH (neutral) and temperature
				(26 °C) for 3 h by varying methylene blue
				concentrations (50-500 mg/1).GAU has
	A State	1		more adsorption efficiency in comparison
	Star I P			to SDC and SD at an initial dye
	1 () () () () () () () () () (wastowater was 100% 02% and 87.1% by
			111	GAC SDC and SD respectively at 50
	0.7 R		101	mg/l dve concentration
Shaohin et	Fly as hand red	Methylene Blue	Batch	Fly ash generally shows higher adsorption
	mud	Wiethy lefter Blue	Baten	capacity than red mud. The results indicate
2005	mad	1.0	100	that the Redlich–Peterson model provides
2005				the best correlation of the experimental
				data The adsorption is lower at pH less
				than 7 and then is increased to higher
	No. Contraction		-	values at pH greater than 7. More
				significant enhancement in the adsorption
		the part and an	1000	of dye is reached at $pH=10$ than at $pH=8$.
Gupta etal.,	Adsorption on	Brilliant Blue	Batch and	The batch studies clearly suggest that both
2006	bottom ash and de		Column	bottom ash and de-oiled soya exhibit
	-oiled soya			almost similar adsorption ability toward
		-		Brilliant Blue FCF and can remove 100 to
				90% of the dye in the concentration range
				0.007 to 0.03 mM, at 30, 40 and 50 °C. The
	1			results obtained are well fitted in the linear
		and the second se	Constant State	forms of Freundlich and Langmuir
				adsorption isotherms. Bulk removal of the
				dye through column operations
				recommends that bottom ash column
				adsorbs quicker and more amount of dye
				(about 95%) than de-oiled soya column
				(about 79%).
Lopez et al.,	Electrochemical	C.I. Reactive	Batch	Ti/PtOx electrodes were used to oxidize
2006	Technique	Orange 4		simulated dye baths prepared with an
				azo/dichlorotriazine reactive dye (C.I.
				Reactive Orange 4). The decolonization
				yield was dependent on the dyeing
				electrolyte (NaCl or Na_2SO_4). Dyeing
	1	1		ensuents which contained from 0.5 to 20

				g/1 of NaCl reached a high decolonization
				g/1 of NaCl reached a high decolonization yield, depending on the current density, immediately after the electrochemical process. These results were improved when the effluents were stored for several hours under solar light. After the electrochemical treatment the effluents were stored in a tank and exposed under different lighting conditions: UV light, solar light and darkness. The evolution of the decolonization versus the time of storage was reported and kinetic constants were calculated. The time of storage was significantly reduced by the application of UV light.
Mall et al.	Adsorption on	Congo Red	Batch	The effective pH ₀ was 7.0 for adsorption on
2006	Bagasse fly ash and activated carbon			BFA. Kinetic studies showed that the adsorption of CR on all the adsorbents was a gradual process. Equilibrium reached in about 4 h contact time. Optimum BFA, ACC and ACL dosages were found to be 1, 20 and 2 g/l, respectively. CR uptake by the adsorbents followed pseudo-second-order kinetics. Equilibrium isotherms for the adsorption of CR on BFA, ACC and ACL were analyzed by the Freundlich, Langmuir, Redlich–Peterson, and Temkin isotherm equations. Error analysis showed that the R–P isotherm best-fits the CR adsorption isotherm data on all adsorbents. The Freundlich isotherm also shows comparable fit. Thermodynamics showed that the adsorption of CR on BFA was most favorable in comparison to activated carbons.
Mane etal., 2007b	Adsorption on rice husk ash	Brilliant Green	Batch	Optimum pH value of 3, adsorbent dose 6 g/l, equilibrium time 5h for the C _o range of 50–300 mg/l. Adsorption of BG followed pseudo-second-order kinetics. Intra-particle diffusion does not seem to control the BG removal process. Equilibrium isotherms for the adsorption of BG on RHA were analyzed by Freundlich, Langmuir, Redlich–Peterson (R–P), Dubnin– Radushkevich (D–R) and Temkin isotherm models using a non -linear regression technique. Langmuir and R–P isotherms were found to best represent the data for BG adsorption onto RHA. Adsorption of BG on RHA is favorably influenced by an increase in the temperature of the operation. Values of the change in entropy and heat of adsorption for BG adsorption on RHA were positive. The high negative value of change in Gibbs free energy indicates the feasible and spontaneous

				adsorption of BG on RHA.
Mane et al., 2007a	Adsorption on bagasse fly ash	Brilliant Green	Batch	Optimum conditions for BG removal were found to be pH 3.0, adsorbent dose 3 g/l of solution and equilibrium time 5h. Adsorption of BG followed pseudo-second- order kinetics. Redliche Peterson and Langmuir isotherms were found to best represent the data for BG adsorption onto BFA. Adsorption of BG on BFA is favorably influenced by an increase in the temperature of the operation. Values of the change in entropy and heat of adsorption for BG adsorption on BFA were positive. The high negative value of change in Gibbs free energy indicates the feasible and spontaneous adsorption of BG on BFA.
Batzias et al., 2007	Adsorption on Sawdust	Methylene blue	Batch	The lower adsorption of BCon BFA. The lower adsorption of methylene blue at acidic pH is due to the presence of excess H^+ ions that compete with the dye cation for adsorption sites. As the pH of the system increases, the number of positively charged sites decreases while the number of the negatively charged sites increases. The negatively charged sites favor the adsorption of dye cation due to electrostatic attraction. The increase in initial pH from 8.0 to 11.5 increases the amount of dye adsorbed.
Minghua et al., 2007	Electrochemical Technique	Cationic red X- GRL; PbO ₂ anode electrode and The cathode was a stainless steel	Batch	At low current density, the performance would be cost-effective but need long treatment time, while at high current density it was of high efficiency but costly. So that, current density of 2.0 mA/cm ² would be a good choice.
Runping et al., 2007	Adsorption on rice husk	Congo Red	Column	Thomas, Adams–Bohart, and Yoon–Nelson models were applied to experimental data to predict the breakthrough curves using non-linear regression and to determine the characteristic parameters of the column
				useful for process design, while bed depth/service time analysis (BDST) model was used to express the effect of bed depth on breakthrough curves. The results showed that Thomas model was found suitable for the normal description of breakthrough curve at the experimental condition, while Adams–Bohart model was only for an initial part of dynamic behavior of the rice husk column. The data were in good agreement with BDST model. It was concluded that the rice husk column can remove CR from solution.

				Freundlich adsorption isotherm models were then applied to calculate thermodynamics parameters as well as to suggest the plausible mechanism of the ongoing adsorption processes. In order to observe the quality of wastewater COD measurements were also carried out before and after the treatments. A significant decrease in the COD values was observed, which clearly indicates that adsorption method offer good potential to remove Congo red from wastewater. Maximum adsorption around 99 and 88% for activated carbon and activated sawdust, respectively, at pH 6.5. Activated sawdust is a cheap and easily available material that thus can act as a better replacement for activated carbon.
Alok et al., 2007	Adsorption on De -Oiled Soya a waste of Soya oil industries and Bottom Ash a waste of thermal power plants	Methyl Orange	Batch and Column	Optimum pH value of 3. Adsorption of the dye over both the adsorbents has been monitored through Langmuir and Freundlich adsorption isotherm models and feasibility of the process is predicted in both the cases. For the two columns saturation factors are found as 98.61 and 99.8%, respectively, for Bottom Ash and De-Oiled Soya with adsorption capacity of each adsorbent as 3.618 and 16.664 mg/g, respectively.
Mittal et al., 2008	Adsorption on bottom ash and deoiled soya	Brilliant Green	Batch	Sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the first order kinetic model for the adsorption of BG by SD. BG adsorbed per unit mass of SD (q_t) increased with the increase in ⁰ C, although percentage BG removal decreased with the increase in C ₀
Mittal et al., 2009	Adsorption on deoiled soya	Congo Red	Batch	Percentage CR removal decreased with the increase in 0 C, although, CR adsorbed per unit mass of SD (q _e) increased with the increase inC ₀
Nandi et al., 2009	Adsorption on Kaolin	Brilliant Green	Batch	Optimum pH value of 7, adsorbent dose 4 g/l and equilibrium time 4 h. The increase in BG sorption capacity with the decrease in temperature has also been reported. The maximum adsorption capacity q_m value of 65.42 mg/g for BG adsorption. The exothermic adsorption. Removal increases with increase in adsorbent dose. Sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the first-order kinetic model for the adsorption of BG.
Lain et al., 2009	Adsorption on CaCl ₂ modified betonies	Congo Red	Batch	Percentage CR removal decreased with the increase in ^{0} C, although, CR adsorbed per unit mass of SD (q_e) increased with the increase InC ₀ .

Panda et al., 2009	Adsorption on Jute stick powder	Congo Red and rhodamine B	Batch	The increase in CR sorption capacity with the increase in temperature. Adsorption kinetics was found to follow a second-order rate expression.
Mittal et al., 2009	Adsorption on deoiled soya	Congo Red	Batch	Percentage CR removal decreased with the increase in ^{0} C, although, CR adsorbed per unit mass of SD (q _e) increased with the increase in ^{0} C.
Ahmad et al., 2010	Adsorption on bael shell carbon	Congo Red	Batch	Adsorption kinetics was found to follow a second-order rate expression. Percentage CR removal decreased with the increase in ⁰ C, although, CR adsorbed per unit mass of SD (q_e) increased with the increase in ⁰ C. The increase in CR sorption capacity with the increase in temperature. The positive value of ΔH^0 indicates that the process is endothermic in nature.
Afkhami et al., 2010	Adsorption on Modified maghemite nano particles	Congo Red	Batch	Adsorption kinetics was found to follow a second-order rate expression. The positive value of ΔH^0 indicates that the process is endothermic in nature.
Hua et al., 2010	Adsorption on cattail root	Congo Red	Batch	Adsorption kinetics was found to follow a second-order rate expression. It seems that the intra-particle diffusion of CR dye into pores is the rate-controlling step in the adsorption process.
Khouni et al., 2011	Coagulation	Blue Bezaktiv S- GLD 150 and Black Novacron R	Batch	Coagulation/flocculation leads to a maximum percent of color removal of about 93% at 593 nm and 94% at 620 nm.
Merzouk et al., 2011	Chemical Coagulation and electro C oagulation techniques	Disperse red dye	Batch and Continuous	Experimental results showed first that Al_2 (SO ₄)3was far more effective than FeCl ₃ for color removal using CC, regardless of operating conditions. A removal yield higher than 90% could be achieved with a 40 mg/l dose of $Al_2(SO_4)318H_2O$ in a large range of pH from 4 to 8 and for a dye concentration up to 235 mg/l. The removal yield could however be enhanced up to 95% using EC for pH values between 6 and 9 at the expense of higher operating costs. Nevertheless, EC presented the additional advantages to be more robust against pH change and to reduce simultaneously equipment costs in comparison to CC.
Lin et al., 2011	Electrochemical Technique	Active Orange 5R	Batch	RuOx–PdO–TiO ₂ /Ti anode possesses higher catalytic oxidation ability, as compared to RuOx–PdO/Ti, in both direct oxidation and indirect oxidation processes. RuOx–PdO–TiO ₂ /Ti could provide a discoloration rate of 98.14% within 30 min, while the COD removal could reach 51.43% in120min. It was indicated that higher electro oxidation ability could be achieved at RuOx–PdO–TiO ₂ /Ti anode.

Rivera et al., 2011	Electrochemical Technique	Reactive Black 5	Batch	The decolorization of an azo dye, Reactive Black 5 (RB5), by an electrochemical technology was studied in both cubic and cylindrical cell configurations, each with a working volume of 0.4 L and graphite electrodes. Low decolorization was detected in the treatment of pure solutions of RB5, but a significant extent of decolorization was observed in the presence of Na ₂ SO ₄ . Nearly complete decolorization was achieved in 3 h for an effluent containing 70 mg/l RB5 and 0.1M Na ₂ SO ₄ , and the TOC removal was approximately 95%. In the presence of the non-inert electrolyte NaCl, complete decolorization was detected. However, due to the chloro-organic compounds formed in the electrochemical oxidation with NaCl, the TOC removal in the most optimal conditions was approximately 93%.
Zhou et al.	Electrochemical	Methyl orange	Batch	High current density enhanced the
2011	Technique	Metnylorange	Batch	High current density enhanced the decolorization on both electrodes, but the promotion on MMO was not as significant as that on the BDD electrode, which led to a sharp increase of specific energy consumption. The decolorization of MO performed better at acidic conditions for two electrodes. High initial concentration enhanced GCE though the COD and TOC removal efficiency was decreased. The GCE on BDD was much higher than that on MMO, indicating that it was much more efficient
Mane et al.,	Adsorption on saw	Brilliant Green	Batch	Adsorption kinetics was found to follow a
2011	dust		2 (second-order rate expression. The adsorption of BG onto SD was found to be exothermic in nature. Adsorbent dose 4 g/L, equilibrium time 3 h for the Orange of 50–300 mg/l. Equilibrium adsorption data for BG on SD were well represented by the R-P and Temkin isotherm models. Adsorption of BG on SD is favorably influenced by a decrease in the temperature of the operation. The adsorption capacities of SD for BG dye were obtained as 58.4795, 55.8659and 52.6315 mg/g at288, 303 and 318 K, respectively. The negative value of ΔG^0 indicates spontaneous adsorption of BG on SD. This study concludes that the SD could be employed as low-cost adsorbent for the removal of BG dye from aqueous solution
Ghaedi et	Adsorption on	Brilliant Green	Batch	More than 90% removal efficiency was
al.,	activated carbon		-	obtained within 30 min at adsorbent dose
2011	prepared from			of 2 g/100ml for initial dye concentration
	acorn			of 25 mg/l. The percentage of dye removal

		remains almost constant within the pH range of around 6–10. The adsorption of dye was found to follow a pseudo-second- order rate equation. Langmuir isotherm model was fitted the best for the adsorption system with an adsorption capacity of 2.11 mg/g of adsorbent. Adsorption capacity
		mg/g of adsorbent. Adsorption capacity increases with temperature.

2. CONCLUSIONS

During the last few years many articles discussed about the adsorption of dyes have been published. This evaluation of literature describe diverse technologies for the removal of a range of dyes from the effluents. The environmental troubles formed by the textile industries have received increased consideration for several decades because of contaminated effluents, which mainly occur from dyeing processes. Lots of colored textiles and leather articles are treated with azo dyes and pigments. This paper presented the effect of various physico-chemical experimental conditions that will affect the dye adsorption such as solution pH, initial dye concentration, adsorbent dosage, and temperature. The most important parameter is the solution pH, where a high pH value is preferred for cationic dye adsorption while a low pH value is more suitable for anionic dye adsorption. For the effect of initial dye concentration due to the saturation of adsorption sites on the adsorbent surface. It was also noticed that the dye removal efficiency increases with increasing adsorbent dosage where the amount of sorption sites available for the adsorption of dye molecules will increase by increasing the dose of adsorbent.

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