STUDIES ON ADSORPTION OF TRIAZINE DYES BY NATURAL AND CHEMICAL MODIFIED AGRO WASTE MATERIALS

Namrata Kaushik , C.P.Kaushik , Ravinder Tuteja , J.K.Sharma
Department of Chemistry, Guru Jambheshwar University of Science & Technology,Hisar – 125001 , Haryana
Email: nkaushik@k.st

ABSTRACT
Triazine dyes an important part of textile dyes are major source of pollution of the environment. Inspite of best efforts being made for their application, exhaustion and fixation on the textile surface, around 20%-30% of dyes remain unused, causing serious problems to aquatic life.The affinities of these dyes to water is very high and it is very difficult to remove the hydrolysed dye from solution, by only physical methods. The use of chemical methods may only replace the dye molecule at the cost of another chemical. These unexhausted organic dye molecules not only aesthetically affect the water but are also potential source of harmful carcinogenic azo amines on reductive degradation. To minimize pollution load the adsorption method is an acceptable technique. Activated Charcoal is an effective surface adsorbent for the removal of soluble dye molecules as surface adsorbent but it is expensive and produces large volume of sludge. Some other agro waste materials have been found to be suitable and viable alternatives to Activated Charcoal. In the present work four different carbon based agro adsorbents are used and studies are carried out to correlate the chemical composition of adsorbents and their relative adsorption with three different triazine dyes. Further, since the triazine dye molecules are anionic in nature, the effect of chemically modified adsorbent surface -both anionic and cationic are also studied and compared.
Key words: *Adsorption, triazine dye, Untreated adsorbents, Modified cationic adsorbents, Anionic adsorbents*

Introduction

Several classes of dyes are available for usage with different types of textile materials. Practically, the important textile dyes can be classified in to acid, basic, direct, disperse, metal complex, reactive, sulphur and vat. Triazine dyes comprise molecules having fibre-reactive groups, such as mono, dichlorotriazinyl and chloroethyl sulphonyl. Dyes are bound to the fibre either through covalent or ionic bonding, van der Waals forces or penetration of colloidal dye particle into the fibre. After dyeing some of the dyes remains unused and is hydrolysed causing pollution load on waste water.

The effectiveness of different decolourisation techniques for the removal of dyes also depends on the dye class (the chromophore) as well as its varying substituent groups (auxochromes). Generally, highly water soluble dyes, i.e. reactive, acid and other dyes are more difficult to remove by conventional techniques than poorly soluble dyes, eg. vat and disperse dyes[1].

In textile dyeing processes a large volume of dye contaminated effluent is discharged. It is estimated that 10%–15% of the dye is lost in the dye effluent[2,3]. The presence of dyes in the effluent even at very low concentrations can be highly visible and undesirable[4,5]. The coloured waste water damages the aesthetic nature of water and reduces light penetration through the water surface[6]. The Triazine dyes, which represent the largest class of dyes used in textile processing, are mostly azo compounds, i.e. molecules with one or several azo (N=N) bridges linking substituted aromatic structures. These dyes are designed to be chemically and photolytically stable. They exhibit a high resistance to microbial degradation and are highly persistent in natural environment. The release of these compounds into the environment is undesirable, not only for aesthetic reasons, but also because many azo dyes and their breakdown products are toxic and/or mutagenic for life [7]. Consequently, the removal of triazine dyes from the effluent is essential, usually through physicochemical methods. In recent years several physico-chemical decolourisation processes have been developed[8,9], such as Membrane-separation[10], Electrochemical[11],Flocculation-Coagulation[12,13] Reverses Osmosis, Ozone oxidation[14], Biological treatment[15-17] Adsorption[18-21]. However these methods are selective, expensive and may need special infrastructure. Decolorisation of effluent by the removal of dyes through a commercially viable method is still a major problem comfronting the textile industry. Among the physico-chemical processes, adsorption technology is considered to be most effective and proven technology having wide potential for applications in both water and waste water treatment[22].

Adsorption has been found to be superior to other techniques for wastewater treatment in term of cost, simplicity of design, ease of operation and insensitivity to toxic substance[23]. Adsorption is primarily a surface phenomenon, which includes utilization of surface forces, leading to concentration of materials on the surface of the solid bodies[24]. In terms basis of strength of binding forces the adsorption may be of two types i.e. physical or chemical adsorption. Physical adsorption involves Van der waals forces and/or hydrogen bonding while chemical adsorption is due to electrostatic forces and covalent bonding.

Adsorption of colour particles from the solution on to the adsorbent surface involves[25]. (i)transport of dye particles from the bulk solution to the exterior surface of adsorbent; (ii)movement of these dye particles across the interface to the external site where adsorption occurs;(iii) migration of adsorbed dye molecules in to the pores of adsorbents;(iv) interactions of dye molecules with interior surface bounding of the pores of the adsorbents; One or more of the above steps may be deciding factors in the treatment of dye effluent for adsorption efficiency in a particular adsorbate-adsorbent system.

Activated carbon has been water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for almost three decades. Since cost is an important parameter in most developing countries, efforts have been made to explore the possibility of using various low cost adsorbents such as sugarcane bagasse, coconut coir pith, saw dust[26], wood charcoal, eucalyptus bark,rice husk, chitin and chitosan[27,28], wheat straw[29], and barley husk, etc.[30-32]. These are biodegradable and are derived from either plant or animal waste, or are industrial byproducts. Most of the adsorbents explored for decolourisation studies are cheap, require little or no processing, are easily available, require little or no processing are and are biodegradable or can be easily disposed by incineration thereby providing a thermal source of energy. Identification of a potential dye adsorbent must be in good agreement with its dye-binding capacity, its regeneration properties, its requirements and limitations with respect to environmental conditions.Unfortunately without prior chemical modification these materials uniformly have very low adsorption capacities for anionic dyes[33].

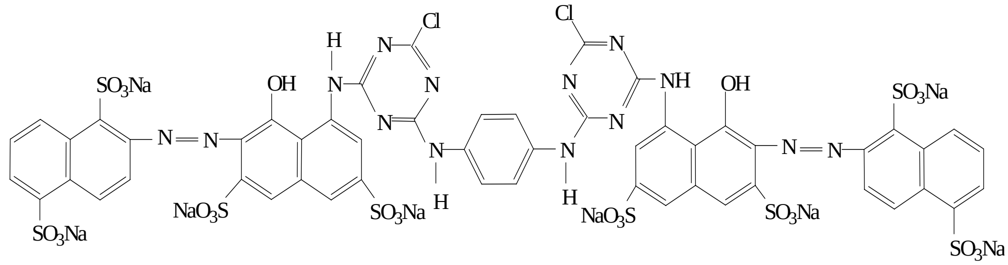
The present study has dual purpose, i.e., finding a solution to the acute problem of water pollution and simultaneously utilizing natural waste material which otherwise have to be dumped. The different adsorbents studied are Activated Charcoal, Sugarcane Bagasse, Coconut Coir Pith, Saw Dust, and Eucalyptus Bark for decolorisation of triazine dye solution. The work also includes the effect of the surface modification chemically and their impact on decolourisation. Chemical composition of adsorbents and mass of dye molecule are also compared.

EXPERIMENTAL

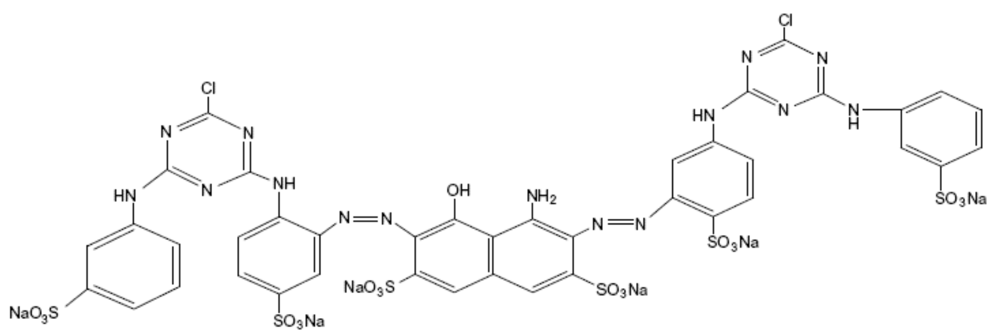
Material & Method:

Dyes:-HE Brand Triazine dyes

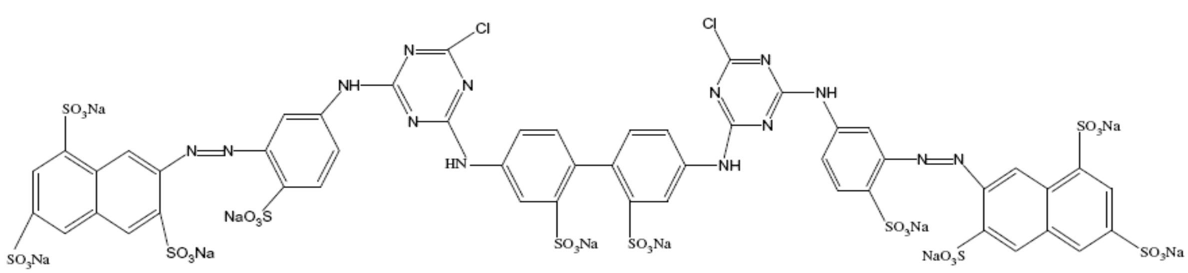
C.I.ReactiveRed141 520 (λ_{max})nm Mol. Wt- = 1772 a.m.u



C.I. Reactive Blue 171 607 (λ_{max})nm Mol. Wt- = 1418 a.m.u



C.I.Reactive Yellow 84 414(λ_{max})nm Mol. Wt- = 1919 a.m.u



All dyes are supplied by Colour division, of Atul India Limited.

Chemicals: 1,2 dichloroethane, methylamine(40% solution), acetic acid, NaOH etc. (L.R. Grade)

Adsorbents:Four agro waste adsorbents are tried:

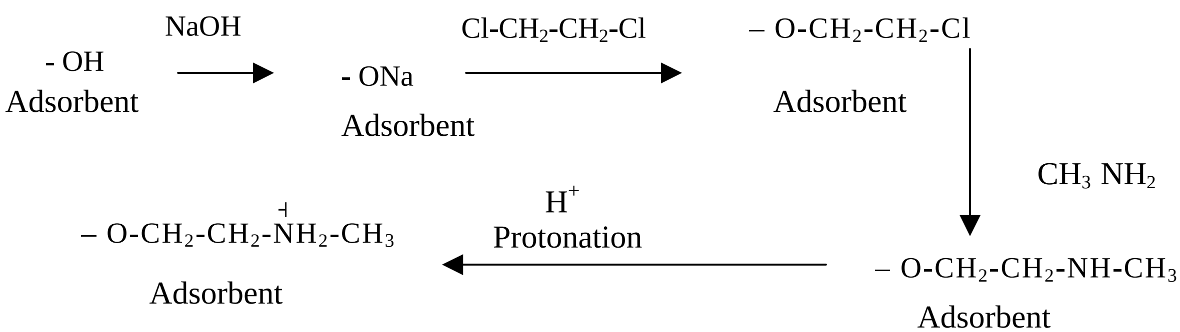
1. Sugarcane bagasse
2. Coconut coir pith
3. Saw dust and

4. Eucalyptus bark

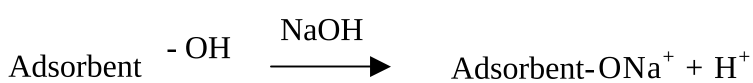
Preparation of Adsorbent: Adsorbents were collected from local market, washed with water, left overnight dipped in water to leach out the colouring matter. Saw dust was filtered and dried well under sun light. The other three adsorbent were chopped into the small pieces, finely grounded, again dried, and sieved to 60 mesh size. Activated carbon 60 mesh size was procured from market.

Chemical Modification of adsorbents:

(a) Cationic Modification –The powdered adsorbents treated with 20% (w/v) sodium hydroxide solution for 5 minute then filtered and treated with 16% (v/v) Dichloroethane in water at 70^0C for 90 minute in a flask. The Dichloroethane treated adsorbent was then rinsed thoroughly with hot and cold water to remove excess of alkali and chemicals. The washed adsorbent was then aminated with the mixture of 10% (v/v) methyl amine and water at a temperature of 70^0 C for the 90 minute again and filtered. The adsorbent was finally treated with dilute acetic acid for protonation.



(b)Anionic Modification:– The powdered adsorbent was treated with20% (w/v) sodium hydroxide solution for five minutes, then filtered and dried before use.



Dye Liquor: Dye solution was prepared by dissolving 0.01% w/v of triazine dye in distilled water.

Method: For each reading 50ml of dye solution was treated with 500mg of finely powdered (60mesh) adsorbent for 30 minute at room temperature in a conical flask with occassionl shaking. After 30 minutes the treated dye solution was filtered off and used for colour density measurement.

Colour Measurement: All colour measurements were carried out with UV spectrophotometer (Elico SL 117) operating in the visible range in absorbance mode. Absorbance values were recorded at the wave length for maximum absorbance (λ_{max}) corresponding to each dye. Dye solutions were calibrated for concentration in terms of absorbance units. Results reported are average of five readings in each case.

Decolourisation efficiency : Decolourisation by adsorbent is calculated by the following formula:

$$\%\ \text{Colour Removal} = \frac{Ab_1 - Ab_2}{Ab_1} \times 100$$

Ab_1 = Absorbance of dye bath originally ;Ab_2 = Absorbance after treatment

RESULT AND DISCUSSION

Adsorption is a surface property of an individual material and depends on the formation of van der waal's forces, hydrogen bond and other electrochemical forces of attraction. The phenomena also depends upon the chemical nature of adsorbate as well as chemical composition , surface structure and porosity of the adsorbent. The adsorption depends upon the resting of dye molecules on surface of adsorbent , penetration of dye molecules into cavities of adsorbent surface and formation of newer attraction forces . Overall it is a physico-chemical process and is coupled with loss of energy and formation of new bonds.

The present work is based on study and compare the adsorption properties of untreated and chemically modified agro adsorbents with three different triazine dye solution. All the adsorbents are naturally occurring agro waste materials and have variable amount of polysaccharides & lignin as major constituents i.e. Cellulose, hemicellulose, lignin alongwith wax, oil and ash contents as impurities. It is interesting to note that in Eucalyptus bark there is no cellulose but tannin is present. Their absorption properties are compared with the results of Activated Charcoal which is organophillic , porous and amorphous in nature and is the best adsorbent. The present work is further extended to chemically modify the adsorbents surface as "cationic" by incorporating a quaternary ammonium ion and as "anionic" by treating with aqueous caustic soda, so as to see the effect on the adsorption of anionic triazine dye species. The role of molecular weight of the dye molecule is also compared in the studies.

Table-1 and Figure –1 represent the result of natural adsorbents with three different type of the dyes. As expected ,the result with Activated Charcoal are best and uniform irrespective of type of dyes, it is about 93% of dye removal. Among the other adsorbent the results are poorest with Eucalyptus Bark which are only about 61% – 63% for these three dyes. The other adsorbents gave moderate results in between the two above ,these are 72% – 84%. It is also noticed that results depends on the size and molecular weight. of the dyes. The R.Blue 171 with smaller molecular size gave better results than R.Red 141 and R.Yellow 84. The results for Sugarcane bagasse varies from 78% – 84% , for Coconut Coir pith it is 73% – 80%, and for Saw Dust these are 72% – 79%.

The results of Table-2 and Figure–2 indicates the results of chemically 'anionic' modified adsorbents. The results are in accordance with the speculation that negative charge on adsorbent surface will repel the anionic dye species and will retard the adsorption. There is a drastic change and adsorption reduced to about 11%-26% only. Again the results are better with the smaller dye molecules. Among the adsorbents the sugarcane bagasse has slightly better results with 20%-26% of dye removal, where as for all others it is even less than 20% of total dye contents. Some amount of dye adsorption is due to the surface property of individual adsorbent and interaction with non charged part of the total surface area. The explanation is also supported with the results of Activated charcoal which is almost unaffected by alkali treatment, as there is no organic part to be chemically modify into anionic species and to effect the adsorption process.

The results of Table-3 and Figure-3 indicate the result of chemically 'cationic'modified adsorbents. As expected the results are extremely good and the removal of dye is 88% or more by these adsorbents, this is due to neutralization of anionic charge of dye molecule with cationic sites on the surface and formation of ionic bond synergic with the usual surface adsorption.The result with activated charcoal are marginally improved to 97% this may be due to the surface entrapping of quaternary ammonium charged species, as such there are no alkyl groups in activated charcoal to be aminate. Both the results with anionic and cationic surface modification are clear indications that adsorption of dye molecules by these adsorbent are not simply a physical process but a physico-chemical phenomena and presence of any charged species on the surface has significant role in the entire process.

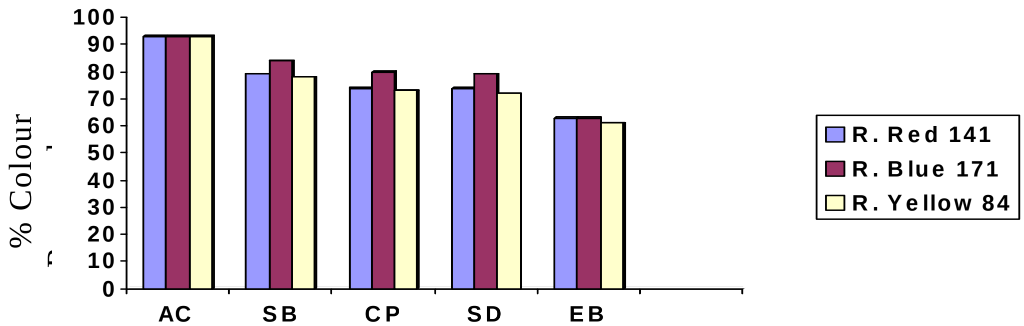


Fig.-1: Decolourisation of Triazine dye Solutions with Untreated Adsorbents

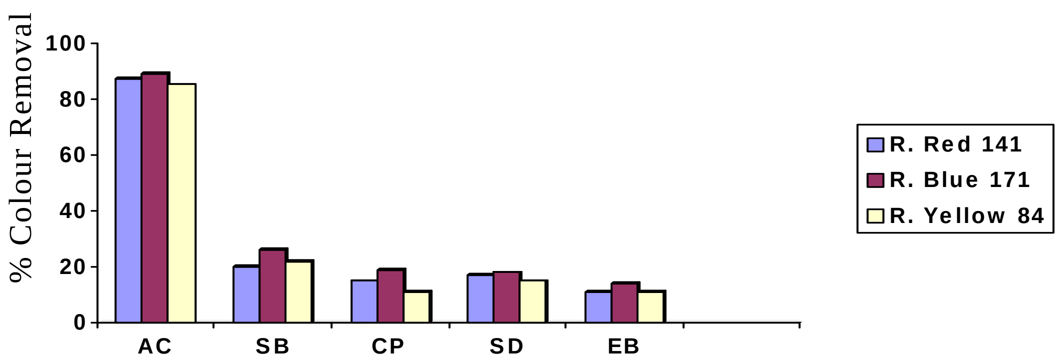


Fig.-2: Decolourisation of Triazine dye Solutions with Chemically Modified Anionic Adsorbents

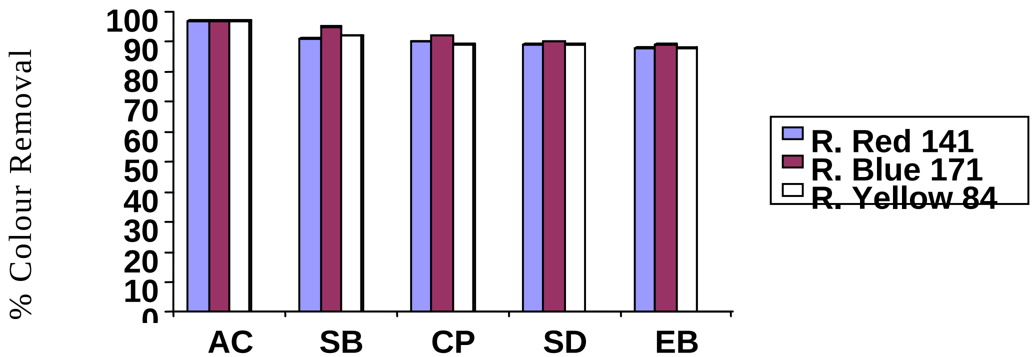


Fig.- 3: Decolourisation of Triazine dye Solution with Chemically Modified Cationic adsorbents

Table-1: Decolourisation of Triazine dye Solutions with Untreated Adsorbents

Dye	Initial Abs	AC		SB		CP		SD		EB	
		Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal
R.Red 141	2.020	0.140	93	0.415	79	0.524	74	0.534	74	0.752	63
R.Blue 171	2.461	0.162	93	0.401	84	0.499	80	0.525	79	0.905	63
R.Yellow 84	1.447	0.101	93	0.315	78	0.390	73	0.412	72	0.562	61

Table-2: Decolourisation of Triazine dye Solutions with Chemically Modified Anionic Adsorbents

Dye	Initial Abs	AC		SB		CP		SD		EB	
		Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal
R,Red 141	2.020	0.256	87	1.610	20	1.723	15	1.670	17	1.804	11
R.Blue 171	2.461	0.260	89	1.832	26	1.999	19	2.009	18	2.115	14
R.Yellow 84	1.447	0.213	85	1.131	22	1.230	11	1.010	15	1.290	11

Table-3: Decolourisation of Triazine dye Solution with Chemically Modified Cationic adsorbents

Dye	Initial Abs	AC		SB		CP		SD		EB	
		Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal	Final Abs	%of Colour removal
R.Red 141	2.020	0.052	97	0.184	91	0.201	90	0.223	89	0.239	88
R.Blue 171	2.461	0.062	97	0.134	95	0.198	92	0.254	90	0.262	89
R.Yellow 84	1.447	0.050	97	0.171	92	0.155	89	0.164	89	0.172	88

It is interesting to note that all the adsorbents have same mesh size and surface area but their adsorption efficiencies are different even for the same dye. The activated carbon is the best compared to the other adsorbents. The less efficiencies of other adsorbents may be due to less porous surface , structural difference and varied chemical composition. The cellulose, hemicellulose, lignin and small amount of other polysaccharides are major components in all adsorbents except , in Eucalyptus Bark where tannin is present in place of cellulose. Among the various components the hemicellulose seems to be good adsorbent being a mixture of pentoses & hexoses sugars and branched in nature which resulted into a more uneven and porous surface structure. Cellulose, a polysaccharide with partial amorphous properties is a fibrous material. The alcoholic groups of polysaccharides acquires a negative charge in water but still it is organophilic and have a tendency to adsorb dye molecules. Lignin is a polymer of aromatic alcohols with phenolic groups , it is hydrophobic and amorphous in nature. The phenolic groups of lignin ionize in water and produces anion , they are more acidic than alcohol. It acts as a adsorbent due to its three dimensional porous structure.Tannin which is present only in Eucalyptus Bark is also a polyhydroxy polyphenol in nature with more number of phenolics groups makes it a poor adsorbent for anionic dye compared to other components. The adsorption of the dye molecules by these agro adsorbents is also enhanced due to significant increase in surface area of adsorbents in (60 mesh) powdered state compared to ungrinded form. The repulsion among negatively charged anion of dye also forces these dye species to diffuse onto the surface and in the cavities to make new bonds with surface particles of adsorbents.

The adsorbate molecule size also plays an important role in adsorption as reported that reactive blue dye 171 has smallest molecular weight and size among the three gave the best results with all adsorbents. The small size makes it possible for more diffusion in surface cavities and mechanical trapping inside along with surface adsorption. The other two dyes with almost same molecular weight and size behaves similarly.

Being the adsorption is a surface property the chemical nature of surface can not be ignored. When the adsorbent surface is ionised and the charge of adsorbate and adsorbent are same i.e. anionic the results are very poor and when the charges on both are opposite i.e. the adsorbent surface is cationic and dye is anionic the results are excellent and comparable with Activated Charcoal irrespective of the adsorbent. This may be possible only when adsorption becomes a chemical phenomena in addition to a surface property.

CONCLUSION

Triazine dyes are an important class of the dyes, in demand for cellulosic materials being they form a covalent bond with substrate, fast and available in wide colour range. Significant work has been done by the scientist to increase its functionality and exhaustion on the substrate but 100% of dye uptake is not possible. The unused dye left out is a potential source of pollution to the environment. For the removal of unused dye the adsorption method with Activated Charcoal is in practice but it is commercially not viable and large volumes of sludge produced is difficult to handle. Agro waste materials as adsorbent are possible alternate to replace the costly activated charcoal, they are carbonaceous, porous and amorphous materials gave encouraging results. Over and above they are biodegradable and hence difficulty of dumping can be avoided. A lot work needs to be done for identifying the nature of interactions between these agro adsorbents and dye molecules, this will help in selecting specific adsorbents for a particular class of dye for optimal results.

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The activist is not the man who says the river is dirty. The activist is the man who cleans up the river.
—Ross Perot