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Recent Modifications of Adsorbent for Adsorption Applications of Dyes

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Abstract—*Adsorption techniques are mostly used to remove dyes from wastewaters. Cheap and eco-friendly adsorbents usage is observed in this review paper which is used for removal of dyes from wastewater. Textile effluent is a cause of significant amount of environmental degradation and human illnesses. Some section describes about the various adsorbents that have been used to remove different types of dyes, such as (Acid green 25, Methylene blue, Reactive Red RN) and their efficiency in the removal of dyes. Paper shows use of the Cationic dye (methylene Blue) twice, first with the chitosan and second with the low cost adsorbent (orange peel/ banana peel/ neem leaves).*

Also Limitation and advantages of some solid adsorbents has been discussed further in this paper. A main attraction of any fabric is color; it goes in river and drains. Its effect on the water of hand pump makes it unhealthy for consumption of human beings. So that's why it is necessary and important to remove these pollutants from waste water. Some introductions and classifications of dye are also mentioned.

Adsorption data obtained in relation to the chemical structures of the dyes, contact time and temperature were shown and also studied a various variety of adsorbent for adsorption process, (Chitosan, Chitosan nanoparticles, Chitosan beads and low cost adsorbent) in this review and discussed all of these.

1. INTRODUCTION

Waste water generate from various sources such as textile industrial area, agriculture, residential areas etc. Different types of dyes are used by different type of textile industries. The dye stuff industry play important role in the growth of the chemical industry. Water consumption in textile industry consumes more than 9000 chemicals in various processes including bleaching, scouring, printing, dyeing, and finishing operations. These are listed in table below [1].

Sr No.	Chemical	Quantity Kg/month
1	Acetic Acid	1611
2	Ammonium Sulphate	858
3	P V Acetate	954
4	Wetting Agent	125
5	Caustic Soda	6212
6	Softener	856
7	Organic Solvent	247
8	Organic Resin	5115
9	Formic Acid	1227
10	Soap	154
11	Hydrosulphites	6563
12	Hydrochloric Acid	309
13	Hydrogen Peroxide	1038
14	Leveling & Dispersing Agent	547
15	Solvent 1425	321
16	Oxalic Acid	471
17	Polyesthylene Emulsion	1174
18	Sulphuric Acid	678
19	Disperse Dyes (Polyester)	1500
20	Vat Dyes (Viscose)	900
21	Sulphur Dyes	300
22	Reactive Dyes	45

In present study authors are focusing on the Pollution control. It is one of the major areas of scientific activity. At present heavy metal and dyes pollution has become worldwide problem; it has grown gradually and is a concern for human health and living organism. Heavy hazards toxicity causes serious health effect such as cancer, organ damage, retarded growth and last case is death. Many adsorbents have been checked for their possibility to lower concentration of dyes from aqueous solutions, such as silica [2], activated carbon [3, 4], chitin [5, 6] and peat [7].

Adsorption with solid adsorbents such as: [8]

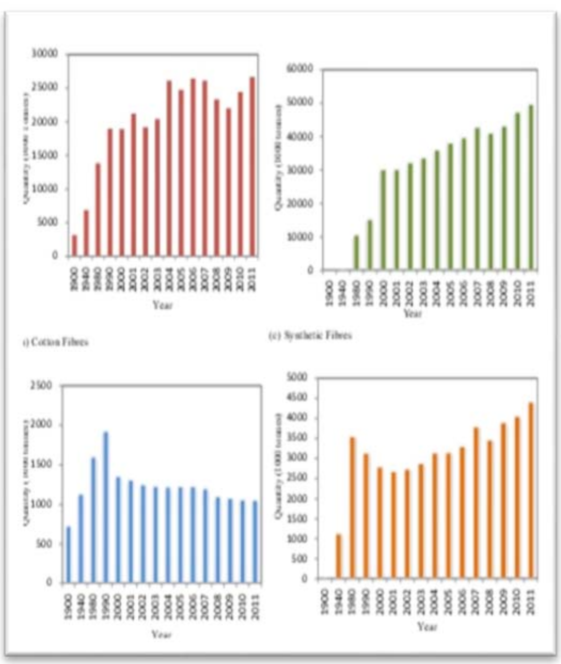
	Advantages	Limitations
Activated carbon	Economically attractive. Good removal efficiency of wide Variety of dyes.	Very expensive; cost intensive regeneration process.

Wood chips / wood sawdut	Effective adsorbent due to cellular structure. Economically attractive. Good adsorption capacity for acid dyes.	Long retention times and huge quantities are required.
Peat	Effective adsorbent due to Cellular structure. No activation required.	Surface area is lower than activated carbon.

The main reasons of these materials being effective for removing dyes from aqueous solution: porosity, high surface area, reactive surface chemistry. According to some studies, it was observed that used adsorbent have high affinity towards positively charged dyes like cationic dyes than the charged negative ones like anionic dyes [9, 10].

Several methods have been developed in this field for discolorations process, such as reverse osmosis, adsorption, ion exchange and, precipitation [11], electrochemical degradation [12], advanced oxidative process [13]. Among all these methods, adsorption has come out as a winner and widely used because it does not require high-tech techniques, is easy to operate and has low cost of application.

One author used cheap adsorbents such as Orange Peel, Neem leaves and Banana peel for adsorption of methylene blue dye, which is also discussed in this review paper. The world production of different textiles during the past century (1900-2011) is shown in Figure, [14].



2. DYE AND ITS CLASSIFICATION

A dye is defined as a colored substance, for textile dyeing almost all the dye compounds are applied. These compounds have some common properties. First, all colored compounds are able to absorb the visible spectrum wave length. Second, they have unsaturated carbon double bond structure so that it causes resonance that can absorb light energy and emits some amount of visible wavelength . These double bonds are called chromospheres such as ethylene, keto, thioketo, azo, anthraquinone etc.

Dye have auxochrome also, basically it is a group of atom to attach the chromophores. This importance is in dyes for providing solubility and cohesiveness [15]. The auxochrome groups are: $-NH_2$ (amino), -COOH (carboxyl), $-SO_3H$ (sulphonate) and -OH (hydroxyl) [16].

On application basis, dyes are classified into different classes. But recently used dyes in textile industry are acidic, basic, disperse, direct, mordant, sulfur, reactive, vat, and azoic dyes. The major anionic dyes are the direct, acid and reactive dye [8]. Below information about these three main dyes are given,

The non-ionic dyes are dispersedyes; it does not ionize in the aqueousenvironment. The major cationic dyes are the azo basic and reactive dyes because of the nitrogen which have free electron pair interact with pi orbital system delocalized.

2.1 Acid Dye

These dyes are water soluble and also called anionic dyes. They contain sulfonic acid functional group; its addition makes dye soluble in water.

2.2 Basic Dye

These are also water soluble dyes, and it's called cationic dyes.

2.3 Direct Dye

These are the generally salt of azo dyes. These dyes are highly soluble in water. Without any addition of mordant these are used in alkaline dye bath [17].

3. PHYSICAL TREATMENT

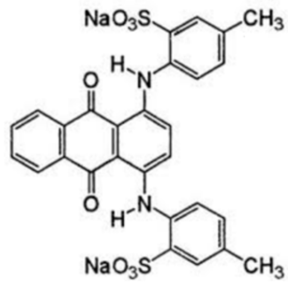
3.1 Adsorption

Now in present day, Adsorption is a popular technique for removal of dye. It is based on the result of two mechanisms, first is ion exchange and second one is adsorption. Adsorbent surface area, particle size, temperature, pH, and contact time have an influence on adsorption process of dye. Amino nitrogen containing adsorbents tend to have a larger adsorption capacity in acid dyes. The most used adsorbent is chitosan, and also other inorganic adsorbents. Discussion on Some low cost adsorbents of agricultural wastes (i.e. peat, coal ashes),is mentioned above [18].

These materials have many advantages due to their widespread availability and cheapness. The regeneration is not necessary sometimes. The 'low cost' adsorbents are profitable for removal of textile dye. Some author's result for adsorption of dyes is summarized in this review.

3.1.1 Adsorption with chitosan/chitosan beads/chitosan nanoparticles

One author described the sorption behavior of acid green 25 on to chitosan. Acid green dye is an anthraquinonic anionic dye, two sulfonic groups present in this dye and also two azoic groups.



Acid Green-25

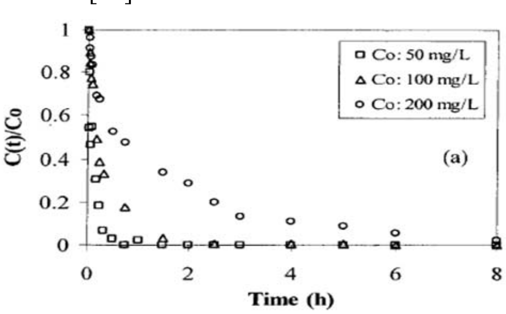
Amine group of chitosan were protonated with below pH 6.5, so the author described in paperfor attraction of anionic sulfonic group, protonation of amine group was necessary. When the pH was controlled during sorption, the optimum pH range was between pH 2 and 5: the sorption efficiency varied by less than 10% to around 75%, this data author mentioned in paper.

3.1.2 Experimental Data

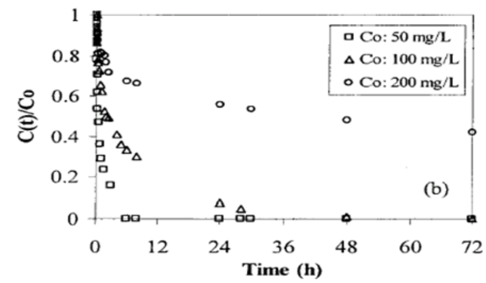
With increasing Acid Green 25 concentration relative to a fixed sorbent amount, strongly increased the time required to reach equilibrium.

For example, although 1–2 h was sufficient to achieve complete recovery of the dye at initial concentrations below 100 mg/L, for the highest concentration (200 mg/L) with raw chitosan 8 was necessary to reach equilibrium and the complete elimination of the dye. [19]

Angham G. Hadi, also studied on chitosan for removal of cationic (i.e. Methylene Blue) dye. In adsorption experiments the stock solution of MB (1.0 g/L) was taken. The desired concentrations ranging from 10 to 60 mg/L were obtained by dilution. For each adsorption experiment, 50 ml of the dye solution with a specified concentration was stirred at 100 rpm in a glass flask. [20]

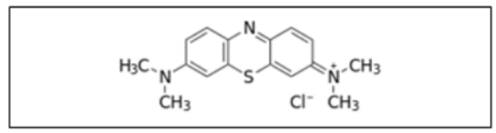


(a)



(b)

Fig. 1: Influence of dye concentration on Acid Green 25 uptake kinetics at pH 3 (pH non-controlled) using raw chitosan (a) and protonated chitosan (b) (Sorbent dosage: 400 mg L_1).



Chemical structure of MB dye

The effect of adsorbent dosage (varied from 0.025 to 0.25 gm) on the percentage removal of 50 mg/L MB solution is shown in Fig. 2. It means, as the adsorbent dosage increased from 0.025 to 0.25 gm the percentage removal of Methylene Blue increased from 26% to 88%, this was because of the increase in the adsorbent surface area and more adsorption sites are available because of increasing adsorbent dosage [21,22]. In adsorption, pH played a role, increased the percentage removal from 25.27% to 89.45% when increased pH from 2 to 8. This was because of the molecular nature of Methylene Blue (cationic molecule).

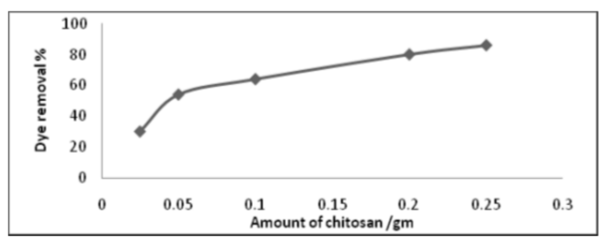
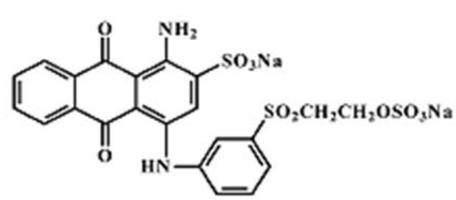


Fig. 2: Effect of adsorbent dosage in MB removal

Antonio R. Cestari et.al, reported in paperReactive Blue RN (blue dye) reacts with chitosan beads and result of adsorption with different contact time from 60 to 120 min by using 23.0 mg/ L pH 2.0 aqueous dye solutions was observed.50 ml solution of known concentration solution, containing was added to 100 mg of the cross-linked beads.



Chemical structure of Blue Dye

Author used this formula for calculating adsorbed dye quantity and also reported when temperature increases, the adsorbed amount decreases. Adsorption of blue dye seems to occur on the beads surface only [23].

$$q = (Na - Ns) / m \quad (1)$$

q= fixed quantity of dye (mg) per gram of beads

Na = quantity of added dye in mg

Ns = dye quantity present at a predetermined time in mg

m= mass of beads in grams

Many authors modified chitosan and prepared chitosan nanoparticles for removal of dyes.

*W.H.Cheung*used used nanochitosan emulsion for experiment. In this experiment volume of nanochitosan suspension (10 ml = 0.030 g) was transferred into 40 ml of dye solutions with predetermined dye concentrations. The flasks were sealed and agitated for 21 days at 200 rpm in the thermostatic shaker bath. Size of nanochitosan (range from 0.0663 μm to 1.763 μm) used as an adsorbent to remove acid dyes, Acid Red 73 (AR73) from aqueous solution. Langmuir, Freundlich and Redlich–Peterson equations used for studying of dye adsorption.

Based on the Langmuir isotherm analysis, the monolayer adsorption capacities were determined to be 2.13 mM/ gram of nanochitosan for Acid Red 73, respectively.

The Redlich-Peterson isotherm equation gave the best correlation for the adsorption of Acid Red 73 with correlation coefficient slightly higher than that of Langmuir model. [24]

3.2 Adsorption with low cost adsorbent (orange peel/ banana peel/ neem leaves)

Numerous researchers worked earlier on variety of adsorbents, the peels and leaves collected and dried at low temperature (<105˚C) for 48 hrs to remove moisture content. After drying, peels were messed to fine powder and sieved through 600 μ size.

20 ml of the stock solution of 1000 ppm methylene blue dye taken and with varied amount (0.2, 0.4, 0.6, 0.8, 1 g) of adsorbent put in to 250ml of above solution and shaking for the time interval of 45 minutes. At the end the Comparative results, it was clearly understood that the Effect of Adsorbent amount plays a very important role in adsorption process for removal of color. Among the three adsorbents, Orange peel found to be very effective next to any other adsorbent. Therefore the efficiency of maximum color removal of Orange peel, Neem leaves and Banana Peel at amount of 1 g for time duration of 45 minutes is found to be 98.76, 97.77 and 97.93 respectively in paper of *Velmurugan.P,* Fig. showing some graphical representation.[25]

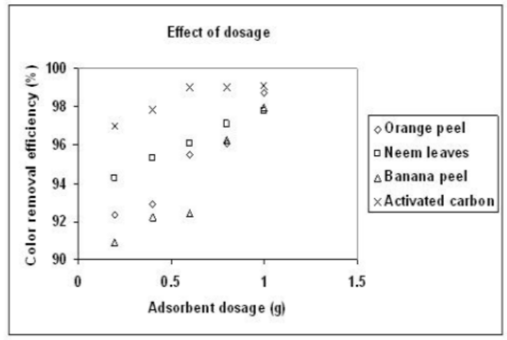


Fig. 3: Comparative results of various Adsorbents on to Effect of Adsorbent Dosage

Author used Freudlich equation, and found that Orange peel has the maximum K value than the other Banana Peel and Neem leaves. The higher value of K (0.775mg/g) proved that the affinity is greater in Orange Peel for adsorption of methylene blue compared with other adsorbents. Author also found the adsorption intention 'n' is 1.50, 0.612 and 1.273 for Orange peel, Neem leaves and Banana peel respectively. K and n are Freundlich constant; 'n' provides a rough estimation of the intensity of adsorption.

It is seen that only Orange Peel and Banana Peel satisfy the heterogeneity condition whereas the other adsorbents do not satisfy this condition.

4. CONCLUSION

Chemicals and dyestuffs used in textile industry does not show the effect on the environment immediately but after a long period of time. In this review some different adsorbent for adsorption of different type of dyes (i.e. anionic and cationic) were used. Some information about chitosan adsorbent also discussed, below the pH 6.5 amine group of chitosan were protonated.

However, one drawback of chitosan as adsorbent is its swelling. For particularly this reason, industrial use has been limited.

During the last three years of time period, A large volume of works has been published, presenting results of chitosan, modified chitosan and some low cost adsorbents for removal of various pollutants (i.e. dyes, metals/ions, others).The majority of works has been already published.

This review paper indicates aboutthe adsorption of dyes using chitosan composites. Chitosan is biodegradable adsorbent, so it's not harmful for the environment.

After studying the adsorption mechanism of acid dye on nanochitosan, it has been observed that first, acid dye gets dissolved and sulfonate group of this dye dissociates and get converted into anionic dye ions. The chitosan amine group became protonated because of H^+ ion.

Due to the electrostatic attraction between amine group of chitosan and negatively charged sulfonate group of acid dye, adsorption process proceeds. Analysis revealed that prepared orange peel was found to be more effective than the Neem leaves and Banana Peel. Experimental studies confirm that these low cost materials can be used as a high cost adsorbent.

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