# Selection of Adsorbent for Removal of Dye from Waste-Water

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***Abstract*— The present article discusses the role of versatile method of adsorption for removal of dye from waste water. An attempt is been made to provide information about the various parameters important in selecting an adsorbent for this purpose. The focus of authors is to provide in depth information about the low cost adsorbents from agricultural waste. The paper also throws light on factors affecting dye removal by adsorption process. Extensive literature has been surveyed and conclusion has been drawn from the studies done, to determine factors affecting the adsorption by agricultural adsorbents.**

***Keywords*— Dyes, Waste Water, Low Cost Adsorbents, Adsorbent selection, Adsorption capacity**

## I. Introduction

Adsorption has been considered as economically favorable, technically feasible and high quality treatment processes for the removal of dissolved pollutants like dyes from industrial wastewater. Around 12% of the synthetic dyes produced are lost during dye manufacturing and processing steps and 20% of this is discharged in the form of waste water. Besides this approximately 50% of the dye is lost after the dying process in textile industries which again contribute 10-15% dyes in the effluent.[1] This significant amount of dye poses a serious problem of water pollution since dye molecules are toxic recalcitrant organic molecule and most of them are stable to heat, light and oxidizing agent. A wide variety of techniques are proposed for removal of dyes from waste water like ion exchange, reverse osmosis, nanofiltration, precipitation, coagulation and adsorption [2]. Among these all techniques, adsorption is very popular due to reasons stated earlier. Commercially available activate carbon is used widely as adsorbent material of choice in many adsorption process but looking at its high cost[3], research is going on for the development of low cost alternative adsorbent. Various researchers have reported the feasibility of using low cost adsorbents derived from natural materials, industrial solid wastes, agricultural by-products and biosorbents [4]. Adsorbents from agricultural waste have been used either as raw adsorbent, after treatment by different physical or chemical processes for improving their adsorption capacity or in the form of precursor for production of activated cahrcoal which were also reported by the researchers [4]. The suitability of agricultural adsorbents is judged on the basis of set of analysis that characterize the physical and chemical surface properties. According to the physico-chemical characteristics and low cost of the agricultural solid wastes, they may be good potential adsorbents [5]. In recent time the intensive use of agricultural waste as adsorbents for dye removal[6] is considered as a very good alternative for disposal of these wastes. The best part is that agricultural wastes usually do not require much prior processing when used as adsorbent. The raw adsorbent from agricultural waste simply require washing, drying, and grinding thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment[7]. Activated carbon derived from different agricultural solid wastes is also used as adsorbent in various studies.[8] Though numbers of articles have been published stating the use of low cost adsorbents from agricultural waste for removal of dyes yet none of these speak about the various parameters needed to be look upon while selecting adsorbents. This paper attempts to provide information about the selection parameters of adsorbents. The effectiveness of various adsorbents and their comparative adsorption capacity is also presented.

There are various factors that needs to be considered while electing an agricultural waste as adsorbent like pore structure, chemical composition of adsorbent and surface chemistry. The chemical compositions of the adsorbent can be inferred by its elemental analysis. From the physical and chemical properties such as BET surface area and functional groups, the adsorption capability of adsorbent can be predicted.

Following types of characterization techniques may be used for adsorbents

- Physical characterization of adsorbents
- Thermal characterization of adsorbents
- BET surface area measurements/ N2 adsorption isotherms
- Pore structure and pore size distribution.
- Scanning electron micrographs
- X-ray Diffraction studies of carbons
- Potentiometric titrations in some cases
- Functional group analysis using FTIR
- X-Ray Photoelectron Spectroscopic Analysis

Methods of Analysis for Physical properties (bulk density, moisture content, solubility in water and acid) and chemical properties (pH, ion exchange capacity) of the prepared adsorbents can also be investigated as per need.

## II. AGRICULTURAL ADSORBENTS

The basic components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing a variety of functional groups. In particular agricultural materials containing cellulose show a potential sorption capacity for various pollutants. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness. The agricultural solid wastes from various cheap and readily available resources such as almond shell, hazelnut shell, poplar, walnut sawdust, orange peel, sawdust, rice husk, sugarcane bagasse, coconut burch waste, and papaya seed have been investigated for the removal of pollutants from aqueous solutions. These agricultural material consists of lignin, cellulose, and hemicellulose, with polyphenolic groups playing important role for binding dyes through different mechanisms. Generally the adsorption takes place by complexation, ion exchange and hydrogen bonding. The functional groups present on the surface of these adsorbents can form complexes or chelates that immobilize the dye moleculesthrough reactions of chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange etc. The agricultural waste materials have been used in their natural form or after some physical or chemical modification. Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), etc. for the purpose of removal soluble organic compounds like dyes and metal from the aqueous solutions have been performed.

In this paper, a wide range of agricultural waste materials as low-cost adsorbent has been presented.

Table I

Agricultural Adsorbents

| Adsorbent | Dye | Maximum Adsorption capacity mg/g) | Refere nces |
|---|---|---|---|
| Bark | Basic red 2 | 1119 | [9] |
| Bark | Basic blue 9 | 914 | [9] |
| Rice husk | Basic red 2 | 838 | [9] |
| Rice husk | Basic blue 9 | 312 | [9] |
| Rice husk | Acid yellow 36 | 86.9 | [10] |
| Rice hull ash | Direct red 28 | 171 | [11] |
| Pine sawdust | Acid yellow 132 | 398.8 | [12] |
| Pine sawdust | Acid blue 256 | 280.3 | [12] |
| Wood sawdust | Basic blue 69 | 74.4 | [13] |
| Wood sawdust | Acid blue 25 | 5.99 | [13] |
| Banana peel | Methyl orange | 21 | [14] |
| Banana peel | Basic blue 9 | 20.8 | [14] |
| Banana peel | Basic violet 10 | 20.6 | [14] |
| Orange peel | Methyl orange | 20.5 | [15] |
| Orange peel | Acid violet | 19.88 | [15] |
| Orange peel | Basic blue 9 | 18.6 | [15] |
| Orange peel | Basic violet 10 | 14.3 | [15] |
| Sugar cane dust | Basic green 4 | 4.88 | [16] |
| Banana pith | Direct red 28 | 5.92 | [17] |
| Neem sawdust | Basic violet 3 | 3.78 | [18] |
| Neem sawdust | Basic green 4 | 3.42 | [18] |
| Wheat bran | Reactive red 180 | 39.42 | [19] |
| Wheat bran | Reactive orange 16 | 34.03 | [19] |
| Wheat bran | Reactive black 5 | 36.03 | [19] |
| Wheat bran | Direct red 80 | 39.15 | [19] |
| Wheat bran | Acid red | 37.76 | [19] |
| Wheat bran | Acid yellow | 199 | [19] |
| pineapple stem (PS | Methylene Blue | 119.05 | [20] |
| Straw | Basic blue 9 | 19.82 | [21] |
| Guava (Psidiumguajava) leaf powder | Methylene blue | 185.2 | [22] |
| Almond shell | Direct red 80 | 90.09 | [23] |
| Pomelo(Citrus grandis peel) | Methylene blue | 344.83 | [23] |
| Broad bean peel | Methylene blue | 192.7 | [23] |
| Peanut hull | Reactive dye | 55.5 | [23] |

The use of these low-cost adsorbents is recommended since they are relatively cheap or of no cost, easily available, renewable and show highly affinity for dyes. The Selection of these agricultural adsorbents is based on following parameters:

A. *Cost:*

The use of agricultural waste as adsorbent material to remove dyes from waste water has become increasingly popular in recent time, because they are less expensive, biodegradable, easily available and efficient. Cost is an important parameter for comparing the adsorbent materials. The cost of an adsorbents varies depending on the degree of processing required and local availability. An adsorbent can be termed as a low-cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from some selected industries. Thus, there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of dyes should be studied in detail

B. *Surface area and Pore Size:*

The surface chemistry of adsorbents has been indicated to have a significant effect on the uptake of various adsorbate molecules. These are important parameters that determine the number and availability of adsorption site for dyes. Surface area and pore size are in inverse relation with each other. The adsorbent with larger surface area have smaller pore size and may not be suitable for adsorption of larger dye molecules due to steric factors. Adsorbents with larger porosity are brittle and can break down easily.

The changes in the surface chemistry of the adsorbents under study can be followed by Potentiometric titrations and data analysis, Solid state 13C NMR, X-ray photoelectron spectroscopy, X-ray powder diffraction (XRD), Braunett-Emett-Teller (BET), Scanning Electron Microscopy (SEM), Thermo-gravimetric analysis (TGA) and Fourier transform infrared spectroscopy etc.

The specific surface area of the adsorbent, pore volume and pore size can be measured by the BET method ($N_2$ adsorption–desorption). The BET equation has been developed to calculate the surface area of a finely divided solid. The equation does neither provide a pore size nor a pore size distribution. What people do to calculate an average pore diameter is to assume to presence of uniform cylindrical pores. The total amount of nitrogen taken up at a pressure of 1 atm and a temperature of 77K gives the total pore volume. With the model of cylindrical pores the total pore volume is 1/4*pi*d*d*l, where d is the mean pore diameter and l is the total length of the pores. If the BET surface area measures the total surface area of the pores the BET surface area S(BET) = pi*d*l. From the two equations l can be eliminated and the average diameter d can thus be calculated. The Barrett-Joiner, Halenda procedure assumes capillary condensation of the liquid nitrogen within the pores and calculates from the relative pressures and the amount of nitrogen taken up at a given relative perssure of the sorption isotherm taking into account the adsorbed layer of nitrogen and the capillary condensed nitrogen the pore size distribution.

The surface images of samples can be obtained using SEM. DTA–TGA can be employed to analyze the population of surface functional groups on the basis of thermal stability. Fourier transform infrared (FTIR) analysis is applied to determine the surface functional groups. XPS helps in interpreting the surface features of the adsorbents.

C. *Densities:*

While selecting adsorbent, three densities are relevant namely bulk density, particle density and apparent solid density. Bulk density is the mass of adsorbent in a specific volume and it is measure using a previously weighed 100mL graduated cylinder and filling it up to 50 mL mark with the adsorbent under study. The cylinder with the adsorbent is weighed accurately. Particle density is the mass of adsorbent per unit volume occupied by the particle. This is accurately measured for cylindrical pores but difficult for distorted shapes. The solid density is mass of adsorbent per unit volume occupied by the particle but with pores deducted.

D. *Nature of Adsorbent Surface:*

Adsorption of dye on adsorbents depend upon the nature of adsorbent surface and type of dyes. In addition to ion exchange ability, the surface charge of adsorbent could be also considered as one of parameters to affect the adsorption process. The point of zero charge (pzc) is defined by the zero charge of surface, at which the sum of positive equals the sum of negative. Depending on the pH value of the aqueous phase, the surface charge of adsorbent could be developed as either positive or negative. If pH (solution) $<$ pzc, the surface is positively charged, and if pH (solution) $>$ pzc, then the surface is negatively.

The adsorptive removal of organic and inorganic substances from wastewater by agricultural adsorbent depends upon the surface area, the pore volume and the pore-size distribution. However, the effectiveness of the adsorption depends not only on the properties of the adsorbent, but also on various parameters (pH, temperature, initial concentration, contact time, particle size of adsorbent, etc.) used for the adsorption process. These parameters should also be taken into account while examining the potential of low-cost adsorbents

## III. PROCESS PARAMETERS AFFECTING ADSORPTION

The effectiveness of adsorption process depends on various process parameters like temperature, nature of the adsorbent and adsorbate, pH, ionic strength, presence of competing pollutant in solution, contact time, adsorbent concentration and other atmospheric and experimental conditions.

*A. pH*

Solution pH plays an important role in controlling the surface charge of the adsorbent, the degree of ionization of the adsorbate in the solution as well as dissociation of various functional groups on the active sites of the adsorbent. In most cases, pH is termed as the 'master variable' The influence of pH on the dye removal can be illustrated on the basis of isoelectric point of the adsorbent surface. Solution pH is a significant parameter that alters the surface charge of the adsorbent, the ionization extent of different pollutants, as well as the structure of the dye molecules. The presence of various ligands such as carboxyl, phosphate and amino group on lignin and cellulose based materials in the ionic state contributes to the reaction with dye ions. At pHzpc, the acidic and basic functional groups no longer contribute to the pH of the solutions. At a pH of the solution below pHzpc the surface of the sorbent is positively charged and can attract anions from the solution. When the solution pH is greater than pHzpc the surface of adsorbent is negatively charged and attract cations.

*B. Effect of adsorbent Dose*

With increase in adsorbent dose the number of available adsorption sites and the surface area increases and hence it results in increase I the amount of dye adsorbed. Although percent adsorption increases with increase in adsorbent dose but the amount adsorbed per unit mass decreases.

*C. Temperature*

The adsorption capacity of adsorbent increases generally with the increase in temperature. The adsorption capacity depends upon thermodynamic parameters like $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$. the positive value of $\Delta H^o$ indicate endothermic nature of adsorption and possibility of physisorption. With increase in temperature, the extent of dye adsorption by physisorption increases and this rules out the possibility of chemisorption. When a finely divided solid is shaken with the polluted water, the pollutants adhere to the solid surface, and a stage of equilibrium is established. At this stage the amount of pollutants adsorbed and in wastewater becomes constant. The relationship, at given temperature, between the equilibrium amount of the pollutants adsorbed and those remaining in wastewater is called the adsorption isotherm. Langmuir, Freundlich and other models are well-known adsorption models by which the adsorption efficiency of the pollutants can be explained in a systematic and scientific way.

*D. Contact time:*

The extent of dye adsorption increase with increase in contact time and decrease with increase in initial dye concentration in general but the amount of dye adsorbed per unit mass increase with initial dye concentration. The extent of adsorption of dye increases with increase in adsorbent dosage. During the adsorption of dyes on the adsorbent surface, first the dye molecule has to encounter the boundary surface and then then diffuse from boundary level film to adsorbent surface and finally to the porous structure of adsorbent.

## IV. CONCLUSION

This paper presented a wide range of information about selection of adsorbents. Inexpensive locally available and effective raw and treated materials could be used in place of costly commercial activated carbon for the removal of dyes from its waste water. From the large number of published literature reviewed here, it is observed that the mechanism and kinetics of adsorption of dyes on various adsorbents depend on the chemical nature of the materials and various experimental conditions like pH, initial adsorbate concentration, adsorbent dosage, and temperature of the system.

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