Decolourisation of Textile Dye House Effluents Using Adsorption – Review

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This article briefly discusses about the applications, ideas, and future perspectives of adsorption process using low cost industrial & agricultural waste available at negligible cost & their application to remove the effluent of textile industry.

Developing countries in Asia are threatened by environmental pollution due to the lack of waste treatment facilities. Most wastewater treatment technologies are known as being costly and not affordable by the municipalities and the small scale polluting industries.

Textile industries discharged a large quantity of highly coloured wastewater effluent which are released into nearby land or rivers without any treatment because the conventional treatment methods are very expensive. On the other hand the low cost technologies don't allow a wishful colour removal and have certain disadvantages. Thus the removal of colour from effluents is one of the major environmental problem. In this concern adsorption process has been found to be more effective method for the treatment of dye containing wastewater.

Coloured dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. There are more than 100,000 commercially available dyes with over 7xl05 tonnes of dyes produced annually. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations whilst 10% was discharged from textile and associated industries. Various physicochemical and biological techniques can be employed to remove dyes from wastewaters. They include the membrane filtration, coagulation/ flocculation, adsorption, ion exchange, advanced oxidation (chlorination, ozonation), flotation, chemical reduction and biological treatment (bacterial and fungal biosorption, biodegradation in aerobic or anaerobic conditions). The technical and economic feasibility of each technique is determined by several factors '(dye type, wastewater composition, operation costs and generated waste products). Also, the use of one individual technique is not sufficient to achieve complete decolorization, therefore dye removal strategies consists of a combination of different techniques. In comparison with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances.

Adsorption is a surface phenomenon that occurs when a gas or liquid solute accumulate on the surface of a solid or liquid forming a molecular or atomic film. Adsorption has been described as an effective separation process for treating industrial and domestic effluents. It is widely used as effective physical method of separation in order to eliminate or lower the concentration of a wide range of dissolved pollutants (organics or inorganics) in the effluent. The adsorptions of various solutes on a solid remain an active area of research. However finding simple and easily performable experiments to illustrate the quantitative aspects of adsorption can be very difficult. The application of adsorption in the removal of highly toxic chromium (vi) which exist in many industrial wastewaters was studied using various adsorbents. For example, a natural adsorbent basalt, andesite and rice hulls have been used successfully.

Adsorption isotherms

The adsorption process is used to remove colour and other soluble organic pollutants from effluent. The process also removes toxic chemicals such as pesticides, phenols, cyanides and organic dyes that can not be treated by conventional treatment methods. Dissolved organics are adsorbed on surface as waste water containing these is made to pass through adsorbent. Adsorption isotherms are known as equilibrium data, are the fundamental requirements for the design of adsorption systems. The Langmuir, Freundlich and Redlich-Peterson isotherms are the most frequently in the literature describing the non-linear equilibrium. The Langmuir isotherm is a theoretical isotherm developed in 1916 (Coulson and Richardson, 1991). This model is based on the few assumptions; all sites are identical and energically equivalent, thermodynamically this implies that each site can hold one adsorbate molecule, adsorption cannot proceed beyond monolayer; the ability of a molecule to be adsorbed at a given site is independent of the occupation of neighbouring sites, which mean, there will be no interactions between adjacent molecules on the surface and immobile adsorption, i.e., trans-migration of the adsorbate in the plane of the surface is precluded. For adsorption of solute from a liquid, the Langmuir isotherm is expressed as Equation (1):

$$q_e = \frac{K_L C_e}{1 + \alpha_L C_e}$$

Where, K_L is the constant related to overall solute adsorptivity (l/g); α_L is the constant related to the energy of adsorption (l/mg). Plot of q_e versus C_e will show a characteristic 'plateau'. The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is 'favourable' or 'unfavourable (Waber and Chakravorti, 1974). Hall et al. (1966) proposed a dimensionless separation factor, R_L as an essential feature of the Langmuir Isotherm which is defined as:

$$R_L = \frac{1}{1 + \alpha_L C_{ref}}$$

Where, C_{ref} is the reference fluid-phase concentration of adsorbate (mg/l) and α_L is the Langmuir constant. For a single adsorption system, C_{ref} is usually the highest fluid-phase concentration encountered. Value of R_L indicates the shape of the isotherm accordingly as shown in Table 1 below:

Table 1: Type of isotherm according to value of R_L

Value of R_L	Type of Isotherm
$0 < R_L < 1$	Favourable
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L = 0$	Irreversible

The Freundlich isotherm is commonly used to describe adsorption characteristics for heterogeneous surface. Derived empirically in 1912 (Metcalf and Eddy, 2003), Freundlich isotherm can be expressed as Equation 3:

$$q_e = K_F C_e^{1/n}$$

Where; K_F is the constant related to overall adsorption capacity (mg/g); 1/ n is the constant related to surface heterogeneity (dimensionless). Therefore, plotting q_e versus C_e yields a nonregression line which permits the determination of 1/n and K_F value of 1/n ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

Kinetics Modelling

Adsorption is time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the dyes in wastewater. In many cases, the kinetics of Equilibrium, Kinetics and Thermodynamic Studies: Adsorption of Remazol Black 5 on the Palm Kernel Shell Activated Carbon (PKS-AC) adsorption based on the overall adsorption rate by the adsorbents is described by the first order Lagergren model and pseudo second-order. The first-order rate expression of Lagergren (Lagergren, 1898; Annadurai and Krishnan, 1997) is given as:

$$\frac{dq}{dt} = k_1 (q_e - q_t)$$

Where q_e and q_t, are the amount of dye adsorbed on adsorbent at equilibrium and time t, respectively (mg/g), and k_1 is the rate constant of first order adsorption (min^{-1}). Integrating equation (4) for the boundary conditions t = 0 to t = t is the following:

$$\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$$

The plot of log (q_e-q_t) versus t will give a straight line and the value of k_1 can be obtained from the slope of the graph.

The second-order kinetic model is expressed as:

$$\frac{dq}{dt} = k_1 (q_e - q_t)^2$$

Where, k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}). The linearised integrated form of (6) is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

The values of q_e and k_2 can be determined from the slope and intercept and there is no need to know any parameters beforehand. The pseudo second-order kinetics model has been successfully applied to several biosorption systems as reported by McKay and Ho, 1999 and Otero et al., 2003.

Thermodynamic Modelling

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be determined by using the following equations:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$

Where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and K_c (L/g) is the standard thermodynamic equilibrium constant defined by q_e/C_e . By plotting a graph of In K_c versus 1/T the values ΔH° and ΔS° can be estimated from the slopes and intercepts.

Factors Affecting Adsorption

The most important factors affecting adsorption are:

- Surface area of adsorbent. Larger sizes imply a greater adsorption capacity.
- Particle size of adsorbent. Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained). However, wastewater drop across columns packed with powdered material is too high for use of this material in packed beds. Addition of powdered adsorbent must be followed by their removal.
- Affinity of the solute for the adsorbent (carbon).The surface of activated carbon is only slightly polar. Hence non-polar substances will be more easily picked up by the carbon than polar ones.
- Number of carbon atoms. For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence formic-aceticpropionic-butyric acid).
- Size of the molecule with respect to size of the pores. Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.
- Degree of ionization of the adsorbate molecule. More highly ionized molecules are adsorbed to a smaller degree than neutral molecules.
- pH. The degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption.

Activated Carbon

Most commonly used adsorbent for treatment is activated carbon. It is manufactured from carbonaceous material such as wood, coal, petroleum products etc. A char is made by burning the material in the absence of air. The char is then oxidized at higher temperatures to create a porous solid mass which has large surface area per unit mass. The pores need to be large enough for soluble organics compounds to diffuse ~n order to reach the abundant surface area. Typical properties of commercially available activated carbon are given in following table.

Table: Properties of typical activated carbon

Parameter	Value
Base material	Lignin
Real density	1.9 g/cm^3
Apparent density	0.244 g/cm^3
Surface area	750m^2/g
Iodine value	93
Effective pore size	2µ

The activated carbon once it is saturated needs replacement or regeneration. Regeneration can be done chemically or thermally. The chemical regeneration can be done in within the column itself either with acid or other oxidizing chemicals. This normally effects partial recovery of activity and necessitate frequent recharging of carbon. For thermal regeneration, the exhausted carbon is transported preferable In water slurry to regeneration unit where it is dewatered and fed to furnace and heated in a controlled condition. This process volatilize and oxidize the impurities held in carbon. The hot reactivated carbon is then quenched with water and moved back to the site. This results in almost complete restoration of its adsorption.

J.T Nawabanne et al studied the biosorption of basic dye from aqueous solution on bamboo based activated carbon in a batch system under various experimental parameters, such as pH, adsorbent dosage, temperature & initial dye concentration. The results showed that these parameters influenced the adsorption capacity. Higher solution pH favoured the adsorption of basic dye. Dye removal increased with increasing temperature of the solution from 25 to 45C, indicating the process to be endothermic. Dye removal increased with increase in the initial concentration of dye. As adsorbent concentration increased, the amount adsorbed per unit mass of adsorbent decreased. Adsorption process using commercial activated carbons is very effective for removal of dyes from wastewater, but its high cost has motivated the search for alternatives and low-cost adsorbents There are some other materials such as sugarcane baggase, rice husk, saw dust, Wheat straw, saw dust, coconut jute, Bagasse ash, activated clay, silica, flyash, etc are also known to be promising adsorbents.

AI-Degs et al. investigated the effect of carbon surface chemistry on the adsorption of three reactive dyes in aqueous solution. In this work adsorption capacity for anionic reactive dyes namely Remazol Golden yellow RNL (reactive Orange 107), Remazol Red RB (Reactive Red 198) and Remazol Black B (Reactive black 5) were determined using Filtrasorb 400 activated carbon. Under the same conditions the adsorption capacity decreases in following manner; Remazol Yellow> Remazol Black> Remazol Red.

The adsorption capacity for reactive dyes increased with a decrease in the carbon particle diameter. At a particle size range of 300-500nm, the values of saturation capacities are reported as 1111,434 and 400 mg g^{-1} for reactive yellow, reactive black and reactive red respectively. F-400 has a high adsorption capacity for these dyes compared to chitosan where reported values are 380,179 and 87 mg g^{-1} for reactive red, reactive yellow and reactive black at a particle size of 250-420mm respectively.

Sugarcane Baggase

Bagasse is the fibrous matter that remains after sugarcane or sorghum stalks are crushed to extract their juice. A typical chemical analysis of bagasse might be (on a washed and dried basis):

Cellulose	45-55%
Hemicellulose	20-25%
Lignin	18-24%
Ash	1-4%
Waxes	<1%

Sugar cane bagasse ash, an agricultural by product, acts as an effective adsorbent for the removal of dyes from aqueous solution. Sachin M. Kanawade investigated the removal of Acid Orange-II from aqueous solution. Adsorbents are very efficient in decolorized diluted solution. The effects of bed depth on breakthrough curve, effects of flow rate on breakthrough curve were investigated with the help of Thomas, Yoon-Nelson model. The removal of dyes at different flow rate (contact time), bed height by Sugarcane Bagasse Ash as an adsorbent has been studied. It is found that percent adsorption of dyes increases by decreasing flow rate from 2 lit/hr to 1 lit/hr, by increasing bed height from 15cm to 45cm.The result shows that, bagasse ash is a good adsorbent for dye effluent treatment.

A.G liew Abdullah et al studied the dye removal of azo dye (methyl red) from aquous simulated wastewater using sugarcane baggase, pretreated with formaldehyde and sulphuric acid. The effects of condition such as adsorbents dosage, initial dye concentration, pH, contact time were studied. The results showed that sulphuric acid treated sugarcane baggase perform well than formaldehyde treated sugarcane baggase, thus making it an interesting option for dye removal from dilute industrial effluents.

Rice Husk

Adsorption is of significant importance for effluent treatment, especially for the treatment of colored effluent generated from the dyeing and bleaching industries. Low cost adsorbents have gained attention over the decades as a means of achieving very high removal efficiencies to meet effluent discharge standards. Anirban K. Chowdhury carried out the batch investigations for color removal from aqueous solutions of Methylene Blue (MB) and Congo Red (CR) using Rice Husk Ash (RHA) as an alternative low cost adsorbent. The performance analysis was carried out as a function of various operating parameters, such as initial concentration of dye, adsorbent dose, contact time, shaker speed, and interruption of shaking and ionic concentration. Performance studies revealed that a very high percentage removal of color was achievable for both dyes. The maximum percentage removal of Methylene Blue was 99.94%, while 98.83% removal was observed for Congo Red. These percentage removals were better than existing systems. Detailed data analysis indicated that adsorption of Methylene Blue followed the Tempkin isotherm, while Congo Red followed the Freundlich isotherm. These isotherms were feasible within the framework of experimentation. Batch kinetic data, on the other hand, indicated that pseudo second order kinetics governed adsorption in both cases. Sensitivity analysis further indicated that the effects of initial dye concentration, shaker speed, pH and ionic strength had no noticeable effect on the percentage dye removal at equilibrium. Batch desorption studies revealed that 50% acetone solution was optimum for Congo Red, while desorption of Methylene Blue varied directly with acetone concentration.

Yupeng Guo et al studied the adsorption of malachite green from aqueous medium by rice husk-based porous carbon. The extent of adsorption was studied as a function of pH, contact time, contact temperature, adsorbate concentration, ion strength & adsorbent with different pore structure. The comparison of adsorption of malachite green on oxidized carbon and their heat treated derivatives were studied. The results obtained under various experimental condition were found to follow the Freundlich adsorption isotherm. The adsorption capacity of carbon activated by sodium hydroxide -activation was larger than that of carbons activated by potassium hydroxide activation.

The adsorption of malachite green on oxidized carbon was decreased and was enhanced after heat treatment.

Saw Dust

Sawdust is a by-product of cutting lumber with a saw, composed of fine particles of wood. Sawdust has a variety of practical uses, including serving as mulch, as an alternative to clay cat litter, as a fuel, or for the manufacture of particleboard. Until the advent of refrigeration, it was often used in icehouses to keep ice frozen during the summer. It has been used in artistic displays, and as scatter. It is also sometimes used to soak up liquid spills, allowing the spill to be easily collected or swept aside. It is used to make Cutler's resin. Mixed with water and frozen, it forms pykrete, a slow-melting, much stronger form of ice. In our review paper we are mainly concentrating on the use of saw dust as an adsorbent for the treatment.

V.K Garg et al studied the removal of methylene blue (basic dye) from simulated waste water using Indian rose wood saw dust. The study investigates the potential use of Indian rose wood saw dust, pretreated with formaldehyde and sulphuric acid, for the removal of methylene blue dye from simulated waste water. The effects of different system variables like adsorbent dosage, initial dye concentration, pH and contact time were studied. The results showed that as the amount of the adsorbent was increased, the percentage of dye removal increase accordingly. Higher adsorption percentage was observed at lower concentration of methyl blue. Optimum pH value for dye adsorption was determined as 7.0 for both the adsorbents. Sulphuric acid treated saw dust or formaldehyde treated saw dust of Indian rose wood can be attractive option for dye removal from dilute industrial effluents.

Pk.Malik studied the adsorption of acid dyes using activated carbons prepared from saw dust and rice husk. The adsorption capacities of saw dust carbons and rice husk carbon were found to be 183 mg & 86.9 mg per gram of the adsorbent respectively. A pH value of 3 is favorable for the adsorption of the acid dyes. The results indicates that the saw dust carbon and rice husk carbons can be employed as low cost alternatives to commercial activated carbon in waste water treatments.

Other Absorbents

Jain et al. described the use of industrial waste products as adsorbents of anionic dyes. In this work a number of low cost adsorbents were prepared from the steel and fertilizer industries. These adsorbents were then used to adsorb three anionic dyes from the water. Their result suggest that inorganic waste such as blast furnace dust, sluge and slag from the steel plants are not suitable for the removal of organic materials, whereas a carbonaceous adsorbents prepared from the fertilizer industry has a good uptake of the anionic dyes which approximated to about' 80% of commercial activated carbon.

Wood has been a source of adsorbent material both in its natural and modified state. The sawdust of a soft spruce wood has been used for the adsorption of basic and acidic dye from solution, finding the removal cost using wood to be only 1.5-8.2% that of commercial carbon. The results show that spruce wood does have an affinity for basic dyes rather than acidic dyes, although uptake is much less than for activated carbon, peats and lignite.

The use of natural and synthetic adsorbents for the removal of colour from effluent has been reviewed. The use of novel alternative adsorbents has continued to attract attention in the literature because of economic considerations, availability and adsorption efficiency. However there is still a need for more detailed information as to the application of the alternatives to carbon in industrial scale processes and to the economic considerations of the alternative adsorption processes. In particular there is need for more research into tailoring the manufacture of specific adsorbents for particular applications together with more general adsorbents with wider applications. Significant research remains to be done into the development of economical and environmentally friendly desorption and regeneration processes.

Almost all the researches has been done on activated material. An effol1 is being done to use low cost industrial & agricultural waste without activation to adsorb the effluents of textile industry.

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