

## **Recent Developments in Preparation of Non Conventional Activated Carbons**

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### **Abstract:**

The present paper has been initiated with a view to investigate the adsorption characteristics of available agro based material to be used as an adsorbent for the removal of the contaminants from the secondary treated industry effluents. The main purpose is to characterise the available agro-based waste material as adsorbent and assess the removal efficiency of contaminants by available agro-based waste material. The paper highlights the various evaluation parameters like initial concentration, time, pH, temperature dose of the adsorbent, particle-size, functional group and agitation speed on the removal of contaminants from the secondary treated industry effluents.

**Keywords:** adsorption, Freundlich, Langmuir isotherms, effluents.

### **1. Introduction**

Water pollution by contaminants from the secondary treated industry effluents like dyes/colours in particular has been a matter of concern for scientific workers since long time. Many of the dyes produce toxic intermediate products during process of removal which are highly toxic. Textile and pulp and paper industries produce large amount of colored effluents. There is no single treatment method which is capable of adequate treatment of the color effluents.

Adsorption is a method which has been widely reported for the removal of dyes from colored aqueous solutions and dye stuff effluents. Activated carbon has been frequently applied for decontamination of colored effluents but its high cost limits its application for large scale treatment of wastewater in developing countries. To reduce the cost of treatment, significant numbers of non-conventional agro-based low-cost adsorbents have been used for the removal of colors from effluents.

### **Classification Of Pollutants In Waste Water And Methods Of Treatment**

The treatment of waste waters from textile industries is carried out in many stages. After pre, primary, secondary treatments waste water still contains dyes and dissolved contaminants which cannot be removed by conventional methods say chemical and biological methods. Such substances can be removed through tertiary polishing treatment processes like adsorption.

Research and development studies have been carried out using activated carbon prepared from number of agricultural wastes and agro based products for the removal of contaminants from the aqueous solutions and are focused on the treatment that are inexpensive and eco-friendly.

Literature review highlights that adsorption through agricultural products such as rice husk, soybean hulls, saw dust, coconut shell, jute, groundnut shell, clay, fly-ash etc., has been demonstrated to be a useful alternative to the conventional treatment systems.

Present work aims at preparation of activated carbon from low cost agro-based waste materials and their subsequent application for the removal of effluent from the secondary treated industrial effluent (live waste water) aqueous solutions.

### **FUNDAMENTALS OF ADSORPTION:**

The surfaces of solids or liquids possess a residual field of force which gives rise to the process of uptake of atoms, molecules, ions from the systems in contact. This phenomenon is known as 'adsorption'.

### **TYPES OF ADSORPTION**

The adsorption is categorized on the basis of interactions involved between the atoms, molecules or ions or adsorbate and adsorbent. According to the forces involved two basic kinds of adsorption processes can be distinguished:

1. Physical adsorption.
2. Chemical adsorption.

## **PHYSICAL ADSORPTION**

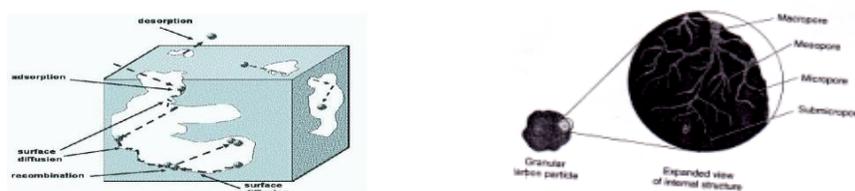
Physical adsorption is reversible and a rapid condition of equilibrium is established between adsorbed and unadsorbed adsorbate species. Molecules adsorbed by physical adsorption are held to the adsorbent surface by physical adsorption are held to the adsorbent surface by weak van der Waals forces of attraction.

## **CHEMICAL ADSORPTION**

This type of adsorption takes place due to the action of specific 'chemical force: i.e. those involved in the transfer or sharing of electrons between an adsorbent and adsorbate species. The chemical reaction on the surface of the adsorbent may be either exothermic or endothermic in nature.

## **ADSORPTION FROM SOLUTIONS**

A solid surface in contact with a solution has the tendency to accumulate surface layer of solute molecules due to imbalance of surface forces. Majority of the molecules accumulated at the interface are adsorbed onto the large surface area within the pores of adsorbent and relatively a few are adsorbed on the outside surface of the particle. **FIG.1.** explains the pore structures of the typical adsorbent.



**FIG.1. Macropore, mesopore, micropore and submicropore adsorption sites on activated carbon.**

## **FACTORS INFLUENCING ADSORPTION**

Molecules of solute are removed from the solution and taken up by the adsorbent during the process of adsorption. The equilibrium distribution of solute between the liquid and solid phases is an important property of adsorption system and helps in defining the capacity of a particular system of equal importance to the engineer are the kinetics of the system which describes the rate at which this equilibrium is reached. The rate of adsorption determines the detention time required for treatment and thus the size of the contacting systems.

The adsorption process takes place in three steps:

1. Macro-transport: movement of adsorbate through water to solid interface by diffusion.
2. Microtransport: Diffusion of organic particles through solid adsorbent.
3. Sorption.

Many factors influence the rate at which adsorption occurs and the extent to which a particular material can be adsorbed. The more important factors are briefly discussed below.

### **Agitation**

The rate of adsorption is controlled by either film diffusion or pore diffusion, depending on the amount of agitation in the system. If relatively little agitation occurs between the adsorbent particle and the fluid, the surface film of liquid around the particle will be thick and film diffusion will be the rate limiting step. If adequate mixing is provided the rate of film diffusion will increase to the point that pore diffusion becomes the rate-limiting step.

## **CHARACTERISTICS OF ADSORBENTS**

Particle size and surface are important properties of adsorbent. The size of adsorbent particle influences the rate at which adsorption occurs; adsorption rates increase as particle sizes decrease. Thus, adsorption rates are faster for powdered carbon than for granular carbon. Adsorption is strongest when the pores are just large enough to permit the molecules to enter.

### **pH**

The pH at which adsorption is carried out has been shown to have a strong influence on the extent of adsorption. Organic acids are more adsorbable at low pH whereas, the adsorption of organic bases is favored at high pH. The optimum pH for any adsorption process must be determined by laboratory testing.

## CONCENTRATION

Commonly both equilibrium amounts adsorbed and rate of adsorption increase with concentration and rate constraints increase with concentration approximately in a linear fashion and the degree of linearity may change in other operating conditions. The extent of adsorption in a given adsorbent depends on the adsorbate concentration in solution. The break points have been interpreted as an indication of either a transition in adsorbed phase or as the on-set of the formation of further types. The actual variation of adsorption with concentration at controlled condition is represented by an isotherm. However, best linear normalization can be made by association of rate constants, obtained from plots of concentration,  $c$ , at time,  $t$ , against  $\sqrt{t}$  as a function of initial adsorbate concentration.

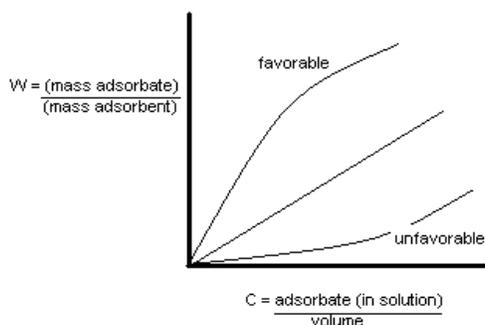
## TEMPERATURE

The temperature at which an adsorption process is conducted will affect both the rate and the extent of adsorption. Adsorption rate increases with increase temperature. However, since adsorption is an exothermic process, the adsorption will increase at lower temperature and decrease at higher temperatures.

Generally the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an adsorption isotherm.

## DEVELOPMENT OF ADSORPTION ISOTHERMS

Adsorption from aqueous solutions involves concentrations of the solute on the solid surface. When solutions contacted with a solid adsorbent, molecules of adsorbate get transferred from the fluid to the solid until the concentration of adsorbate in solution is in equilibrium with that on the surface and no change can be observed in the concentration of the solute on solid surface or in the bulk solution. Equal amounts of solute eventually are being adsorbed and desorbed



simultaneously. This is called adsorption equilibrium.

FIG.2.ADSORPTION ISOTHERMS

Adsorption equilibrium data is typically plotted in the form of an *adsorption isotherm* (i.e. at constant temperature) with the mass adsorbed on the y-axis and the mass in the fluid on the x-axis as in FIG.3. The shape of the curve is significant and factors heavily into design. "Favorable" isotherms permit higher solid loadings at lower solution concentrations. These tend to start out steep and level out. Isotherms which start out flat are "unfavorable", since they only work well at high concentrations of solute. Several fits have been proposed for isotherms.

The shape of the adsorption isotherms gives qualitative information about the adsorption process and the extent of the surface coverage by the adsorbent. All isotherms share a number of common features. These data can then be used for the preliminary evaluation of the proposed system.

Various mathematical relationships have been developed to describe the dynamic equilibrium distribution of adsorbate between the adsorbent and bulk liquid phases. These relationships are applicable when the adsorption tests are conducted at constant temperature and are referred to as adsorption isotherms. Freundlich, Langmuir and BET adsorption isotherms are the most commonly used models for describing the dynamic equilibrium.

## FREUNDLICH ADSORPTION ISOTHERM

Freundlich developed an empirical equation or the adsorption isotherm which encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. This equation can also be explained to the varification of adsorption with concentration over a limited range at constant temperature. The Freundlich adsorption

isotherm can be expressed as:  $q_e = K_F C_e^{1/n}$

$\log q_e = \log K_F + 1/n \log C_e$

Plot of  $\log q_e$  versus  $\log C_e$  gives straight line with intercept  $\log K_F$  and slope  $1/n$

Where,

$q_e$  = amount of dye adsorbed per unit of adsorbent (mg/g)

$C_e$  = Equilibrium concentration of dye in (mg/L)

$K_F$  = Quantity of dye adsorbed for unit concentration of dye in (mg/g ) and

$1/n$  is the measure of adsorption intensity Value of  $1/n$  from plot indicates good adsorption potential. Value of  $1/n$

obtained is always less than 1. For steep slopes ( $1/n$  close to 1) indicate high adsorptive capacity at high concentrations.

For flat slopes ( $1/n$  close to 0) indicate less adsorptive capacity at lower concentrations.

### LANGMUIR ADSORPTION ISOTHERM

The basic assumptions underlying Langmuir's model which is also called the ideal localized monolayer model are:

1. The molecules are adsorbed on definite sites on the surface of the adsorbent.
2. Each site can accommodate only one molecule (monolayer). The area of site is fixed, quantity determined solely by the geometry of the surface.
3. The adsorption energy is the same at all types, and
4. The adsorbed molecules cannot migrate across the surface or interact with neighboring molecules.

The Langmuir equation was originally derived from kinetic consideration. The Langmuir isotherm can be expressed as:

$$C_e/q_e = 1/ab + 1/a (C_e)$$

A plot of  $C_e/q_e$  versus  $C_e$  gives straight line with intercept  $1/ab$  and slope  $1/a$ .

### BET Adsorption Isotherm

Brauer, Emmett and Teller developed the BET adsorption isotherm for the generalization of the ideal localized monolayer treatment (Langmuir Model) to account for multilayer adsorption. The BET model is based on the assumption that each molecule in the first adsorbed layer serves as site for adsorption of a molecule into the second layer serves as a site for adsorption of a molecule into the second layer and so on. The BET equilibrium isotherm can be represented by:

$$q_e = \frac{K_B Q^0 C_e}{(C_s - C_e)[1 + (K_B - 1) C_e/C_s]}$$

OR

$$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{K_B Q^0} + \frac{K_B - 1}{K_B Q^0} \frac{C_e}{C_s}$$

Some of the other important adsorption isotherms are Redlich-Peterson Isotherm and Henry's Law Linear Adsorption Isotherm.

Henry's Law Linear Adsorption Isotherm represents the simplest isotherm in which the amount adsorbed varies directly with the equilibrium concentration of solute. The isotherm is described by:

$$Q_e = K_h C_e$$

The isotherm is obtained under conditions at micro and trace concentrations solute. Adsorption thermodynamic parameters can be obtained from adsorption equilibrium constants with temperatures. Linear regression is frequently used to determine the best-fitting isotherm. The linear least-squares method with linearly transformed isotherms has also been widely applied to confirm experimental data and isotherms using coefficients of determination.

### Methodolgy

#### ADSORPTION PRACTICE

Experimental determination of the isotherm is a standard practice for determining the feasibility of an adsorbing system, selecting the adsorbent for evaluating the dose of the adsorbent. Batch experiments are to be carried out to obtain the equilibrium adsorption data for all the contaminants in this work.

Many investigators have employed the adsorption which is carried out either in a batch wise or in a continuous manner. The review reflects on various types of Batch adsorption system and continuous flow systems.

### 1. Batch Adsorption Systems

In a batch process the adsorbent and wastewater are mixed together in a suitable reaction vessel until the concentration of adsorbate has been reduced to the desired level. Separation of adsorbent (through filtration, centrifugation or settling leaves an effluent suitable for discharge and the adsorbent itself can be regenerated and reused or discarded).

The number and size of adsorption vessels and the amount of adsorbent needed to achieve the required degree of treatment must be determined for the design of batch adsorption systems. These are influenced by wastewater volume, flow rate, and the rate of the adsorption reaction.

Most batch adsorption systems are operated on a fill and draw basis and are limited to small wastewater volumes, flow rate, and the rate of the adsorption reaction. For small volumes generated over a period of 8-10 hours only one adsorption vessel is used.

Batch absorbers can be operated either as a single or as a multistage units operating in counter-current fashion.

### 2. Continuous Adsorption Systems

The continuous flow processes are usually operated in fixed bed adsorption columns. These systems are capable of treating large volumes of wastewaters and are widely used for treating domestic and industrial wastewaters. These columns may be operated either as single unit or as multiple units in parallel or series or combined parallel and series. Furthermore, they may be separated either in the up-flow or down-flow modes. Up-flow columns can also be used as extended or fluidized beds. In moving bed absorbers (Pulse bed absorbers), bed of adsorbent particles move downward and removed from the bottom and an equal volume of fresh adsorbent is added to the top.

Down-flow beds also remove suspended solids through filtration. Such dual purpose units have lower capital cost than separate units.

#### Adsorption Column Design

Continuous column studies for investigating the effects of bed heights, flow rate and initial concentration of contaminants. For designing an unsteady state fixed bed adsorber, model is needed that predicts the solute concentration in the bed as a function of time and position. The rate of adsorption depends upon external mass transfer, internal diffusion and surface adsorption.

#### Breakthrough Curves

Breakthrough point and breakthrough curve are of significant importance in adsorption studies and designing the operating conditions. The area of the activated carbon bed in which the sorption occurs is called Mass Transfer Zone (MTZ). As top layer of the carbon granules become saturated with organic materials, the MTZ will move further down in the bed until breakthrough occurs.

The curve of the pollutant concentration as a function of time has an S shaped appearance and is commonly called the breakthrough curve as shown in the FIG 3. It shows typical breakthrough curve. The time at which the breakthrough curve first begins to rise appreciably is called the break-through point and the time at which the outlet effluent concentration essentially reaches that of the inlet pollutant concentration is called the exhaustion point. The shape of the mass transfer zone depends on the adsorption isotherm, flow rate, and the diffusion characteristics. Usually, the shape is to be determined experimentally.

In designing a column, the length of the adsorption zone represents the minimum bed depth needed to produce a low solute concentration in the effluent. The actual bed depth is usually greater than this minimum to allow a reasonable operating period between regeneration of the adsorbent.

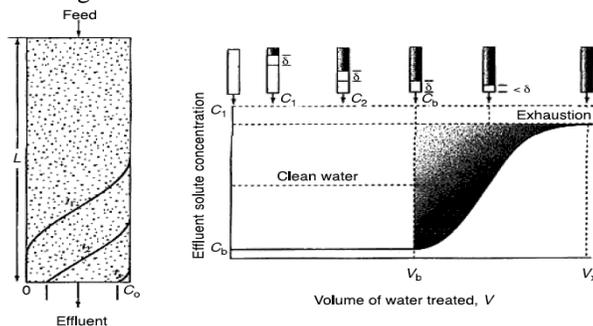
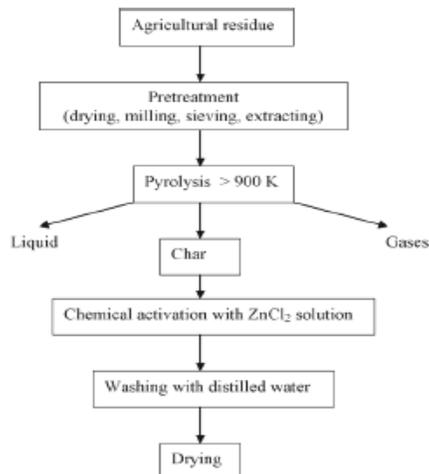


Fig 3. Typical Breakthrough Curve Showing The Movement Of Mass Transfer Zone.

### **Adsorbents:**

Activated carbon is to be prepared by making a char from the organic materials such as coconut shell or walnut hulls or jute. The char is produced by heating the base material to a red heat (less than 700°C) in a retort to drive off the hydrocarbons, but with an insufficient supply of oxygen to sustain combustion as shown in **FIG. 5**.

**FIG. 5** Process Flow Diagram Of Preparation Of Activated Carbon From Agricultural Waste



### **Analytical Procedure**

The analysis involves evaluate the effects of various operating parameters and establish the equilibrium constants by Batch adsorption studies. The tests are to be conducted in temperature controlled conditions in various concentrations, maintaining agitation speed for a fixed time up to equilibrium. The supernatant liquid is to be analyzed for dyes spectrophotometrically. Adsorption equilibrium data is to be typically plotted in the form of an adsorption isotherm to define the various constants. The effects of various operating parameters to be studied are:

#### **1.EFFECT OF CONCENTRATION AND TIME**

The initial adsorbate concentration and time of between the adsorbate and adsorbant are significant importance as the rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of the adsorbent for its use in the waste water treatment.

#### **2.EFFECT OF pH**

The pH at which adsorption is carried out shows a strong influence on the extent of adsorption. This is partly due to the fact that hydrogen ions themselves are strongly adsorbed partly because the pH influences the ionization, and adsorption of many compounds. Organic acids are more absorbable at low pH whereas, the adsorption of organic bases is favored at high pH. The optimum pH for any adsorption process must be determined by laboratory testing.

#### **3.EFFECT OF AGITATION SPEED**

If relatively little agitation occurs between the adsorbent particle and the fluid, the surface film of liquid around the particle will be thick and film diffusion will be the rate limiting step. If adequate mixing is provided the rate of film diffusion will increase to the point that pore diffusion becomes the rate-limiting step.

#### **4.EFFECT OF TEMPERATURE**

The temperature at which an adsorption process is conducted will affect both the rate and the extent of adsorption. Adsorption rate increases with increase temperature. However, since adsorption is an exterior process, the adsorption will increase at lower temperature and decrease at higher temperatures.

For evaluating the above parameters effluent solutions of different concentrations were agitated with known amounts of adsorbents till equilibrium is attained.

### Adsorption Kinetics

Kinetics of adsorption is quite significant as it decides the residence time of adsorbate at solid solution interface and helps in determining the rate of the adsorption process. This study includes

1. Adsorption Rate study and
2. Intra-particle diffusion study.

#### 1. Adsorption Rate study :

The review of the literature reveals that rate of uptake of adsorbate by adsorbent is of significant importance for the control of efficiency of effluent treatment and for designing the adsorption system. The rate equation for transfer of adsorbate from fluid to solid phase depends upon the nature of interaction between adsorbate and adsorbent process. The rate constants of the adsorption to be determined using first order rate expression proposed by Lagergren:

$$\text{Log}(q_e - q) = \text{log } q_e - K_{ad} / 2.303 \cdot t$$

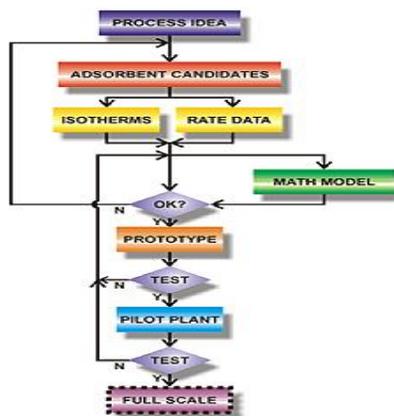
Where,  $K_{ad}$  is the rate constant for adsorption

The straight line plots of  $\text{Log}(q_e - q)$  versus time  $t$  for adsorption of dyes are to be plotted to check for validity and check if it obeys first order rate kinetics. The rate constant can be determined from the slopes of the plots.

#### 2. Intra-particle Diffusion study :

The kinetics of solute transport from solution phase to the surface of adsorbent particles is either by film diffusion, pore diffusion, pore surface diffusion or the combined effect of the above. The analysis involves plots of adsorbate and adsorbed per unit mass of the adsorbent versus square root of time. The plots should be linear and pass through the origin. The profile of the graph indicates whether the process is controlled by film diffusion or intra-particle.

FIG 5. Flow-Chart Presentation Of Adsorption Kinetics



### Thermodynamic Parameters

The adsorption reaction at any interface between two phases can be regarded as an equilibrium process. The point of equilibrium is being dictated by the relative energies. These energy values can be defined in terms of thermodynamic parameters like free energy, enthalpy and entropy changes.

The free energy of an adsorption, considering the adsorption equilibrium constant  $K_a$  is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a$$

Where,

$\Delta G^\circ$  is free energy, standard free energy change (J/mol),  $R$  is the universal gas constant (8.314 J/mol K), and  $T$  is the absolute temperature (K).

The literature reveals that the negative values of **free energy** indicate the spontaneous nature of adsorption. Thermodynamic parameter, **free energy** could be calculated from adsorption equilibrium constant obtained from langmuir isotherm. The value of **enthalpy and entropy** could be obtained from the slope and intercept of the relationship between **free energy** and reaction temperature.

$$\Delta H^\circ = R(T_2/T_1/T_2 - T_1) - \ln(K_2/K_1)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ) / T$$

If the value of **enthalpy** is positive, indicates that the adsorption reaction is endothermic. Thermodynamic considerations of an adsorption process are necessary to indicate whether the process is spontaneous or not. The free energy change is an indication of spontaneity of a chemical reaction and therefore is an important criterion for assessing the adsorption process. The enthalpy and free energy changes indicate exothermic nature of adsorption. The entropy change suggests the randomness in the adsorption.

### Implications

From both environmental and economical considerations, converting these waste materials into more valuable products such as activated carbons for water treatment like dye removal is an attractive option, as it offers a solution to two environmental issues simultaneously. This paper aims to highlight the feasibility of converting these non-conventional waste materials to activated carbon for removing dyes from wastewater.

The main aim is to use live waste water from one of the industries say textile or paper and pulp industry for the removal of contaminants for the utilization, reuse and recycle to meet the requirement of the non potable water as a solution for water scarcity in the industrial sector.

## **References**

1. Metcalf and Eddy waste water treatment disposal and reuse 4th edition, Tata McGrawHill publication.
2. Saini D. R. Feb 2010 Activated carbon adsorbant for pollution control Journal of Indian association for environmental management, vol-37-1, P 51-64.
3. Industrial Waste water Treatment, A.D.Patwardhan, Prentice-Hall, New Delhi.
4. Ayhan Demirbas, Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review Journal of Hazardous Materials 167 (2009) 1–9
5. Ö. Yavuz\*, A. H. Aydin, Removal of Direct Dyes from Aqueous Solution Using Various Adsorbents Polish Journal of Environmental Studies Vol. 15, No. 1 (2006), 155-161.
6. S. Saiful Azhar, Dye Removal from Aqueous Solution by using Adsorption on Treated Sugarcane Bagasse American Journal of Applied Sciences 2 (11): 1499-1503, 2005
7. Manfred Clara, Birgit Strenn, Ernis Saracevic, Norbert Kreuzinger Adsorption of bisphenol-A, 17 $\beta$ -estradiol and 17 $\alpha$ -ethinylestradiol to sewage sludge Chemosphere 56 (2004) 843–851.
8. Y.C.Sharma and S.N.Kaul, Adsorption of Methylene Blue from Aqueous Solutions by an Economically Viable Indigenous Activated Carbon. Environmental Sanitation
9. Shikha Chandra. Gaikwad.S, Decolorization of Pulp-Paper Mill Effluents by Endophytic strains Bacillus spp and Pseudomonas spp of Mimosa pudica, using Batch Reactor.
10. Ageetha and P. Sivkumar Adsorption of Cr (VI) and Pb (II) from Aqueous Solution Using Agricultural Solid waste, Journal of Environ. Sciences and Engg. Vol- 51, No-2, P 151-156, April.
11. Suresh K, Borah M Adsorption of Nickel by Bentonite Clays: A Comparative Study Journal of Environmental Sci. and Engg. Vol 51 – 2, 133-136, April 2009.
12. S.Renganathan, Kinetic studies on sorption of Basic Dye using EICHORNA CRASSIPES, 13.Y.C. SHARMA, UMA S.N. UPADHYAY and F. GODE Adsorptive Removal of Basic Dye from water and wastewater by Activated Carbon, Volume 4, Number 1: 21-28, January-April, 2009, Journal of applied sciences and Journal of Environmental Sci. and Engg.
14. G.H.Sonavane, V.S.Shrivastav, Removal of Basic Dye (Methylene Bl) from Aqueous Solution by Adsorption, Journal of Environmental Sci. and Engg. Vol 51 – 1, 45-52, Jan 2009.
15. Yao-hui Huang, Chan-Li Hsueh, Chun-Ping Huang, Liang-Chih Su, Adsorption thermodynamics and kinetics studies of Pb(II), Separation and Purification Technology. Vol 55 (2007) 23-29.