

STATE OF ART OF BIOSORPTION TECHNIQUE FOR TREATMENT OF HEAVY METALS BEARING WASTES

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ABSTRACT

Adsorption is one of the Physico-chemical treatment methods, used in treating water and waste water. Activated carbon is commonly used as an adsorbent for treating the raw waste. But the cost of activated carbon is high; hence this method is not adopted in treatment plants. Adsorption process is possible to remove dissolved solids, B.O.D., C.O.D., Colour, heavy metals, organic acids etc. The prospects of using many low cost materials [available mostly as agricultural, commercial and industrial waste] as adsorbents for pollution abatement have been investigated extensively in recent years. The non conventional adsorbents process remarkable adsorption capacity for the removal of heavy metals like Cd, Cr, Cu, Fe, Hg, Mn, Ni and Pb, surfactants, dyes, colour, organics from the industrial and municipal effluent.

This paper represents the review of past work on removal of heavy metals by biosorption by using low cost adsorbents in natural and modified forms. Attempts are also made to cover all methodology and techniques for the removal of heavy metals, BOD, COD and TDS.

KEYWORDS Adsorption, biosorption, heavy metals, low cost adsorbents, isotherms

1.1 INTRODUCTION

During the 1970's increasing environmental awareness and concern led to a search for new techniques capable of inexpensive treatment of polluted wastewaters with metals. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on binding capacities of various biological materials. Till date, research in the area of biosorption suggests it to be an ideal alternative for decontamination of metal containing effluents. Biosorbents are attractive since naturally occurring biomass adsorbents or spent biomass can be effectively used. Biosorption is a rapid phenomenon of passive metal sequestration by the non-growing biomass/adsorbents. Results are convincing and binding capacities of certain biomass/adsorbents are comparable with the commercial synthetic cation exchange resins.

The biosorption process involves a solid phase (sorber or biosorber; adsorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (adsorbate, metal). Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. There are many types of adsorbents; Earth's forests and plants, ocean and freshwater plankton, algae and fish, all living creatures, that including animals are all "biomass adsorbents". The renewable character of biomass that grows, fuelled directly or indirectly by sunshine, makes it an inexhaustible pool of chemicals of all kinds.

Biosorption has advantages compared with conventional techniques (Volesky, 1999). Some of these are listed below:

- Cheap: the cost of the biosorbent is low since they often are made from abundant or waste material.
- Metal selective: the metal absorbing performance of different types of biomass

can be more or less selective on different metals. This depends on various factors such as type of biomass, mixture in the solution, type of biomass preparation and physicochemical treatment.

- Regenerative: biosorbents can be reused, after the metal is recycled.
- No sludge generation: no secondary problems with sludge occur with biosorption, as is the case with many other techniques, for example, precipitation.
- Metal recovery possible: in case of metals, it can be recovered after being sorbed from the solution.
- Competitive performance: biosorption is capable of a performance comparable to the most similar technique, ion exchange treatment. Ion exchange is, as mentioned above, rather costly, making the low cost of biosorption a major factor. Biosorbents intended for bioremediation environmental applications are waste biomass of crops, algae, fungi, bacteria, etc., which are the naturally abundant. Numerous chemical groups have been suggested to contribute to biosorption. A review of biosorption of heavy metals by microorganisms is presented below.

Biosorption by microorganisms have various disadvantages, and hence many low cost adsorbents (industrial/agricultural waste products/byproducts) are increasingly used as biosorbents. This chapter also provides review of the low cost adsorbents used for removal of heavy metals (Ahalya *et al.*, 2004).

Chromium compounds are widely used in the leather, textile, chemical manufacture, metal finishing and many other industries. However, at higher concentrations all compounds of chromium are toxic and causing adverse effects on plants and aquatic life. Thus it becomes imperative to remove chromium from industrial effluents before discharging into water or onto land. Number of chemical and physical treatment methods is available but these treatment processes require more capital investment, recurring expenditure and consequently they are not suitable for small scale industries

Keeping in view the low cost investment, easiness in operation, removal of all types of metals, removal of organic matter and colour, physico-chemical treatment viz., adsorption (by using low cost adsorbents) process is highly effective and cheap. Hence in this project work the past literature review of different papers of different authors has been presented for the removal of heavy metals from industrial effluents or from the aqueous solution using adsorption process.

1.2 REMOVAL OF Cr, Cu, Al, Pb, Cd AND Zn

O. A. Ekpete, F. Kpee, J. C. Amadi and R. B. Rotimi et. al,(2010)studied the removal of heavy metal ions Cr (VI) and Zn (II) from aqueous solution using the skin of orange peel (*Citrus sinensis*) as an adsorbent under different experimental conditions

was in this study. The concentrations of the metal ions adsorbed were determined by atomic absorption spectroscopic (AAS) method. The parameters investigated were temperature, contact time, adsorbent dosage, initial metal ions concentration and pH. It was observed that the white inner skin of orange removed more of Cr (VI) than Zn (II) metal ions in all the adsorption experiments. The optimum removal of the Cr (VI) and Zn (II)metal ions occurred at pH 3 and at temperature 30°C. Application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 8.068 (mg/g) and 1.078 (mg/g) for Cr (VI) and Zn (II)metal ions respectively.

O. K. Olayinka, O. A. Oyedeji and O. A. Oyeyiola et. al, (2009)The study investigated the adsorption of Cr(VI) and Ni(II) on modified coconut husk (low cost adsorbent) for the remediation of Cr(VI) and Ni(II) from some synthetic industrial waste effluents. The coconut husk was modified by mixing with 0.1 M NaOH and HCl respectively. The effects of varying adsorbent loading, hydrogen ion concentration, contact time and temperature of adsorption were studied. Similar experiments were carried out using unmodified coconut husk, in order to compare the results obtained from the modification experiments. The result showed that the HCl modified adsorbent gave 96% ± 3.6 removal for Cr(VI) at a pH of 4.0 while about 99% ± 0.7 of Ni(II) was removed at a higher pH of 7.0. The unmodified adsorbent gave a 90% ± 8.8 adsorption for Cr (VI) and 97% ± 1.5 for Ni(II) respectively. However, the NaOH modified adsorbent gave the least adsorption of 40% ± 9.9 for Cr (VI) and 80% ± 6.1 for Ni(II). The equilibrium data for the adsorption of Cr(VI) and Ni(II) on coconut husk was tested using both the Freundlich and Langmuir adsorption isotherms. The Freundlich isotherm was found to be more suitable for Cr(VI) adsorption, while the Langmuir isotherm was observed to be better for Ni adsorption on coconut husk. To evaluate the mechanism of adsorption, pseudo-first order and second order kinetic models were used. The adsorption mechanism was found fit the second order. The HCl modified adsorbent gave the best result for removal of Cr (VI) from synthetic industrial effluents.

R.P Singh, N. Gupta, R. Suman and Radha Gupta et. al, This paper discusses a study aimed to evaluate the feasibility of using powdered activated carbon prepared from agro-wastes for the removal of heavy metals from electroplating effluents. During the

study, batch tests were conducted using an electroplating industry effluent that contained 18.0, 18.9, 8.6 and 15.6 ppm of Cr(VI), Ni(II), Cu(II) and Zn(II) respectively. The ability of coconut coir carbon (CCC), Sagaun Sawdust Carbon (SSC), wheat stem carbon (WSC) and rice husk carbon (RHC) to remove heavy metals from the effluent was studied. The removal was in the order of Ni > Zn > Cu > Cr over a wide range of initial concentrations: 1-20 mg/l at sorbent dose 1 g/l, pH 4.8, temperature 25°C, rpm 250 for five hours (5 h). The sorption increased with increasing contact time but the equilibrium was attained in two hours for Cr, 3.0 h for Cu, 3.5 h Zn and 4 h for Ni. The order of metal removal capacities for these chemical sorbents was: RHC > CCC > WSC > SSC. Electroplating effluent showed 4 to 10 % lower removal as compared to synthetic standard solution under similar conditions.

Mohd. Ajmal, Ali Mohammad, et al. (1998) studied the adsorption behavior of cadmium, zinc, nickel and lead from aqueous solutions by mangifera indica seed shell. Authors conducted the batch adsorption studies at different temperatures. Adsorption increase with contact time and equilibrium attained in 90 of Zn, Ni and Pb at 6.0 and thereafter increase in pH resulted to decrease in percent removal. In case of Cd(II), the maximum removal was found when the temperature was between 30-40°C, but above 40°C the desorption of the adsorbate increase may be due to weakening of adsorptive forces between active sites of the adsorbents and the adsorbate species and also between the adjacent molecules of adsorbed phase. Adsorption of Cd(II), Zn(II), Ni(H), and Pb(II) at pH 5.0, obeyed the Freundlich equation than the Langmuir equation. The calculated Freundlich constants (In k) are >1, at all the temperature range (30-50°C), indicated that the ions Zn, Ni and Pb are strongly adsorbed on the adsorbent. Finally authors studied the effect of salinity by adding NaCl (0.25-9.0gms. / 50 ml) on the adsorption of Cd, Zn, Ni and Pb. It was found that the presence of NaCl reduces the adsorption in all cases, may be due to relative competition between Na ions and Cd, Zn, Ni and Pb species on the active adsorption sites of Mangifera indica seed shell.

Saravanane, Sundararajan, et al(1998) studied the adsorption of Cu(II), Mn(II), Fe(II) and Cd(II) on saw dust, rice husk and chemically modified saw dust and rice husk. Rice husk and saw dust is activated by treating 3 parts of it (by weight) with 1 to 2 parts of EDTA or activated carbon and keeping it in a hot air oven at a temperature of 140-160°C for a period of 24 hrs. It was washed well with water to remove the traces of free acid and then dried at 105-110°C and then activated at a higher temperature of 800-850°C for a period of 30 minutes. It was saw dust Posses greater adsorption capacity for all metals than rice husk. Chemically modified saw dust could remove 98.28% of Cu(H), 100% of Mn(II), 96.72% of Fe(II) and 96.72% of Cd(II) from the waste. Both the chemically treated rice husk & saw dust are very efficient for the removal of metals. It was found that the copper & cadmium adsorption are effective at pH 4 to 6, manganese at pH 7.0 and the iron at pH between 3 to 4. Removal of Cu (II), Mn(II), and Cd(II) increases from 28 mg/g to 48mg/g when the

concentration of metal ion increases from 30 to 100 mg/l for all metals over a pH range of 2 to 9. It was also observed that the equilibrium attained within 2 to 3 hours and is independent of the initial concentration. Authors concluded that the activated carbon as an activator is found to be superior to EDTA for saw dust and rice husk and the process of uptake obeys both Langmuir and Freundlich isotherms.

Gupta, Srivastava, et al (1997) used activated carbon developed from fertilizer waste for the removal of Hg(II), Cr(VI), Pb(II) and Cu(II). The raw material was a waste product collected from National Fertilizer Limited (NFL) was converted into activated carbon and the particles of size 200-250 mesh were selected. Parameters selected for the studies are length of the primary adsorption zone (PAZ), total time involved for the PAZ, time for PAZ to move down its length (t_d), amount of adsorbate adsorbed in PAZ from break point to exhaustion, time of initial formation of PAZ (t_i), etc. From the experimental results authors found that the total time for PAZ to establish itself, move down the length of the column and out of bed is least for Hg(II) and maximum for Cu(II) while Pb (II) and Cr (VI) falls in between. Similar is the trend for t_d and t_i . The time required for the movement of zone down its own length in the column is that in between 2 to 4 hrs. The time required for the formation of initial PAZ in between 1 to 2 hrs. The percent saturation at break point is 79.2, 75.0, 66.6 and 64.3% for Hg^{2+} , Pb^{2+} , Cr^{6+} and Cu^{2+} respectively. Exhausted adsorbent can be regenerated by applying 50.0 ml NH_4OH for almost complete desorption of chromium and 80.0 ml of 2M HNO_3 for lead. Authors are considered the cost of the adsorbents and found that the cheapest variety of commercially available carbon in India costs Rs. 10750/ton where as fertilizer waste costs about Rs. 860/ton including cost of conversion into activated carbon.

Tiwari., Pramod *et al.* (1989) worked on the removal of toxic metals such as Cr(VI) and nickel from dilute solutions resulting from electroplating industries by using an activated carbon in the pH range of 5.5 to 8.0. Results showed that the removal of chromium decreases with the increase in pH and a sudden decrease in removal from 88% to about 40% when the pH increased from 5.5 to 7.0. This is further reduced from 40 to 27% when the pH is raised from 7.5 to 8.0, whereas in case of Cu and Ni, percent removal increases with the increase in pH.

Singh & Mishra *et al.* (1992) used saw dust coated with the iron hexamine gel for the removal of certain heavy metals such as Hg(II), Pb(II), Cr(VI), Ni(II), Cd(II) and Cu(II). This modified adsorbent exhibits good adsorption potential for Hg(II), Pb(II), and Cr(VI), and significant uptake of Ni(II), Cd(II) and Cu(II) but poorer capacity for Zn(II) and Mn (II).

Bhalke, Tripathi *et al.* (1999) studied the uptake of heavy metals including fertile uranium and fission products strontium and cesium by using sunflower plant dry powder at pH 2.5, 4.0 and 7.5. The heavy metals are taken up by the plant to significant levels ($K_b > 10$ mg/l at pH 7.5). The distribution coefficient (K_d) value for Sr is higher at pH 2.5 than that at pH 4.0 and 7.5. Other elements such as Pb, Zn,

Cu, Cd have lowest K_d values at pH 2.5 and highest at 7.5 in the descending order.

M. Rao *et al.* (1999) studied the removal of various pollutants from its aqueous waste by adsorption using various low cost adsorbents. Such as rice husk, carbon, rice straw, bagasse, coconut jute, tea powder, saw dust, fly ash, groundnut husk, hair etc. has been studied by various authors for the removal of heavy metals are presented in this paper. Authors stated that the high cost of conventional activated carbon forced to conduct intensive research to identify the low cost adsorbents. Adsorption is dependent on various controlling factors such as pH, temperature, adsorbent dose and its characteristics, adsorbate concentration agitation speed, contact time, size and shape of adsorbent molecules.

1.3 REMOVAL OF CHROMIUM

P. Venkateswarlu, M. Venkata Ratnam, D. Subba Rao and M. Venkateswara Rao *et. al.* (2007) In this paper presented investigation, *Azadirachta indica* (neem) leaf powder is used as an adsorbent for the removal of chromium from aqueous solutions. The equilibrium studies are systematically carried out in a batch process, covering various process parameters that include agitation time, adsorbent size and dosage, initial chromium concentration, volume of aqueous solution and pH of the aqueous solution. Adsorption behavior is found to follow Freundlich and Langmuir isotherms. The adsorption mechanism is described by a Pseudo second order kinetics.

V. Vinodhini and Nilanjana Das *et. al.* (2009) presented the adsorption of chromium(VI) ions from aqueous solutions has been investigated on Neem sawdust (NS), Mango sawdust (MS), Wheat shell (WS), Sugarcane bagasse (SB) and Orange peel (OP). The adsorbent which showed highest chromium (VI) removal was Neem sawdust. The influence of pH, contact time, biomass dosage and initial metal concentration on biosorption was investigated. The biosorptive capacities of the biosorbents were dependent on the pH of the chromium solution, with pH 2 being optimal. The adsorption data fitted well with the Langmuir isotherm model. The adsorption capacities were found to be 58.82, 37.73, 28.08, 23.8 and 19.80 mg/g for NS, MS, WH, SB and OP, respectively.

S. Arivoli, P. Martin Deva Prasath and M. Thenkuzhali *et. al.* (2007) has presented a carbonaceous adsorbent prepared from an indigenous waste by acid treatment was tested for its efficiency in removing chromium ion. The parameters studied include agitation time, initial chromium ion concentration, carbon dose, pH and temperature. The adsorption followed first order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plots were 11.51, 11.69, 12.00 and 12.57 mg/g respectively at an initial pH of 7.0 at 30, 40, 50 and 60°C. The temperature variation study showed that the chromium ion adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the chromium ion solutions. Almost 65% removal of chromium ion was

observed at 600C. The Langmuir and Freundlich isotherms obtained, positive value, pH dependent results and desorption of dye in mineral acid suggest that the adsorption of chromium ion on BC involves physio-sorption mechanism.

Tariq S. Najim and Suhad A. Yassin et. al. (2009) they presented Modified pomegranate peel (MPGP) and formaldehyde modified pomegranate peel (FMPGP) were prepared and used as adsorbent for removal of Cr(VI) ions from aqueous solution using batch process. The temperature variation study of adsorption on both adsorbents revealed that the adsorption process is endothermic, from the positive values of ΔH . These values lie in the range of physisorption. The negative values of ΔG show the adsorption is favorable and spontaneous. On the other hand, these negative values increases with increase in temperature on both adsorbents, which indicate that the adsorption is preferable at higher temperatures. ΔS values showed that the process is accompanied by increase in disorder and randomness at the solid solution interface due to the reorientation of water molecules and Cr(VI) ions around the adsorbent surface. The endothermic nature of the adsorption was also confirmed from the positive values of activation energy, E_a , the low values of E_a confirm the physisorption mechanism of adsorption. The sticking probability, S^* , of Cr(VI) ion on surface of both adsorbents showed that the adsorption is preferable due to low values of S^* ($0 < S^* < 1$), but S^* values are lower for FMPGP indicating that the adsorption on FMPGP is more preferable.

S.H. Hasan , K.K. Singh , O. Prakash , M. Talat , Y.S. Ho et. al. (2007) there paper presented Novel biosorbent 'maize bran' has been successfully utilized for the removal of Cr(VI) from aqueous solution. The effect of different parameters such as contact time, sorbet concentration, pH of the medium and temperature were investigated and maximum uptake of Cr(VI) was 312.52 (mg g⁻¹) at pH 2.0, initial Cr(VI) concentration of 200 mg L⁻¹ and temperature of 40 °C. Effect of pH showed that maize bran was not only removing Cr(VI) from aqueous solution but also reducing toxic Cr(VI) into less toxic Cr(III). The sorption kinetics was tested with first order reversible, pseudo-first order and pseudo-second order reaction and it was found that Cr(VI) uptake process followed the Pseudo-second order rate expression. Mass transfer of Cr(VI) from bulk to the solid phase (maize bran) was studied at different temperatures. Different thermodynamic parameters, viz., ΔG° , ΔH° and ΔS° have also been evaluated and it has been found that the sorption was feasible, spontaneous and endothermic in nature. The Langmuir and Freundlich equations for describing sorption equilibrium were applied and it was found that the process was well described by Langmuir isotherm. Desorption studies was also carried out and found that complete desorption of Cr(VI) took place at pH of 9.5.

Suresh Gupta, B. V. Babu et. al. (2009) has presented continuous adsorption experiments are conducted using fixed-bed adsorption column to evaluate the performance of the adsorbent developed (from activated tamarind seeds) for the removal of Cr(VI) from aqueous solutions and the results obtained are

validated with a model developed in this study. The effects of significant parameters such as flow rate, mass of adsorbent, and initial Cr(VI) concentration are studied and breakthrough curves are obtained. As the flow rate increases from 10 to 20 mL min⁻¹, the breakthrough time decreases from 210 to 80 min. As the mass of adsorbent increases, breakthrough time gets delayed. The breakthrough times are obtained as 110, 115 and 210 min for 15, 20 and 25 g of activated tamarind seeds. As the initial Cr (VI) concentration increases from 100 to 200 mg/l, the break point time decreases from 210 to 45 min. The process parameters for fixed-bed adsorption such as breakthrough time, total percentage removal of Cr(VI), adsorption exhaustion rate and fraction of unused bed length are calculated and the performance of fixed-bed adsorption column is analyzed. The mechanism for Cr (VI) adsorption on activated tamarind seeds is proposed. At low value of solution pH (= 1), the increase in Cr (VI) adsorption is due to the electrostatic attraction between positively charged groups of activated tamarind seeds and the HCrO₄⁻. A mathematical model for fixed-bed adsorption column is proposed by incorporating the effect of velocity variation along the bed length in the existing model. Pore and surface diffusion models are used to describe the intra-particle mechanism for Cr(VI) adsorption. The breakthrough curve obtained theoretically from pore diffusion model and surface diffusion model are compared with experimental results for different operating conditions. The standard deviation values obtained for pore diffusion model and solid diffusion model are 0.111 and 0.214 respectively.

Chandra W. Purnomo, and Agus Prasetya et. al. (2007) The breakthrough curves of Cr(VI) on bagasse fly ash (BFA) at room temperature were measured in a fixed-bed apparatus. It has been tried to fit the experimental data to fixed-bed model for breakthrough curve. Then the effective diffusivity of hexavalent chrome ion was obtained. The effective diffusivity can be used to predict breakthrough curves at other adsorption conditions. The material characterizations have been conducted before the adsorption experiments.

Gautam K. Nagda and Vikram S. Ghole et. al, (2009) discussed about Tendu leaf biomass, a waste from local bidi industry was chemically treated to obtain an activated carbon and tested for its ability to remove hexavalent chromium from aqueous solution. The new activated carbon was prepared by treating tendu waste with glutaraldehyde. It was characterized by scanning electron microscopy, porosimetry and BET surface analyses and other physico-chemical methods. Its ability to remove chromium from aqueous solution was tested and compared with commercial activated carbon. Adsorption parameters, kinetics and isotherm studied in batch experiments showed that the new carbon has maximum adsorption capacity for chromium as 108.34 mg g⁻¹, while commercial carbon has that of 113.9 mg g⁻¹. The adsorption process followed Pseudo-first order rate kinetics and fits well with Langmuir isotherm. The newly developed carbon from tendu waste offers viable alternative for commercial activated carbon

and removal of toxic chromium from aqueous solution is a promising eco-friendly technique.

M. Venkata subbaiah, S. Kalyani, G. Sankara reddy, Veera m. Boddu and A. Krishnaiah et. al, (2008) Removal of chromium(VI) from aqueous solution was studied using abundantly available *trametes versicolour polyporus* fungi as biosorbing medium under equilibrium and column flow conditions. Various sorption parameters such as contact time, effect of pH, concentration of Cr(VI) and amount of biomass on the adsorption capacity of the biosorbent were studied. The equilibrium adsorption data were fitted to Freundlich and Langmuir adsorption isotherm models and the model parameters are evaluated. In addition, the data were used to predict the kinetics of adsorption. The results indicated that the adsorption of Cr(VI) on fungi followed second order kinetics. The column flow adsorption data were used to predict break through curves. The fungi loaded with Cr(VI) was regenerated with 0.1 M NaOH solution and the regenerated biomass was used in the subsequent adsorption-desorption cycles. The experimental results demonstrated that the *trametes versicolour polyporus* fungi could be used as sorbent for immobilizing Cr(VI).

B.V. Babu and Suresh Gupta et. al, describe the kinetic behavior of a fixed-bed adsorber can be explained and the characteristic breakthrough curve of the adsorption phenomena can be obtained through mathematical models. In the earlier models, the kinetics is explained using a mathematical model that takes into account of external and internal mass transfer resistances with a non ideal plug flow behavior. The variation of fluid velocity along the column is an important aspect, which has not been accounted so far. In the present study, a mathematical model is proposed for explaining the kinetic behavior of adsorption phenomena incorporating the fluid velocity variation along the column length also. Internal mass-transfer resistances due to pore diffusion mechanism are considered in the model. The proposed mathematical model for fixed-bed adsorption is solved numerically and compared with earlier model reported in literature. The results show that the breakpoint is obtained earlier which represents the realistic behavior in adsorption phenomena. Initially the sharp front of the breakthrough curve is seen followed by broadening of tail of the breakthrough curve. Simulations are carried out using the present model for a systematic parametric study. The effects of various important and influencing parameters such as flow rate, bed height, inlet adsorbate concentration and particle diameter on breakthrough curve are studied in detail. Shri Chand, Agarwal et al (1994), studied the removal of Cr(VI) using four kinds adsorbents such as raw bagasse, activated bagasse carbon, bagasse ash and activated coconut jute. Authors used batch experiments and found that 1-5 hrs. time was adequate to reach equilibrium state and a maximum removal of hexavalent chromium i.e. 99.25% was obtained with coconut jute carbon at an adsorbent dose of 12 gm/l. Further it was found that adsorption capacity of coconut jute carbon is much superior at all pH level, hence it can be used at natural pH

conditions in the waste treatment plants. Efficiencies of adsorbents for Cr(VI) removal at natural pH (4.38) by coconut jute carbon, activated bagasse, raw bagasse and bagasse ash are 97.5, 61.40 and 30% respectively. The effect of initial concentration of adsorbate showed that 97% of Cr(VI) was removed when an initial concentration of Cr(VI) was 30 mg/lit and pH 2.0.

Manju and Anirudhan (1990) investigated the removal of Cr(VI) using coconut fibre pith (CFP). Batch adsorption studies were used to determine the effect of adsorbent dose and adsorbate concentration. Maximum removal of hexavalent chromium was found in first two hours and equilibrium attained in 3 hours. Also it was found that percentage Cr(VI) removal reduced from 99.2% to 87.39% with an increase in initial concentration of Cr(VI) from 50 to 200 mg/l. It was reported that this percentage reduction may be due to the fact that for a fixed adsorbent dose, the total available sites are limited thereby adsorbing almost the same amount of chromium. Authors concluded that the process is exothermic and the maximum Cr(VI) removal occurs at pH 2.0 and the thermodynamic parameters have been calculated and the adsorption data fits the Freundlich isotherm equation. They also reported that the spent carbon can be regenerated by washing carbon with 1M NaOH.

Raji and Anirudhan (1998) used saw dust charcoal for the removal hexavalent chromium. Batch experiments were carried out and observed that at pH 2.5 and temp 30°C, the equilibrium state for the removal of Cr(VI) reaches within 210, 240, 270 and 300 min. for an initial concentration of 50, 75, 100 and 150 mg/l respectively. With the increase in initial concentration of Cr(VI) from 50-150 mg/l, the uptake of Cr(VI) increases from 95.2% to 86.1% at pH 2.5 and 30°C. This is due to the percentage uptake is dependent on initial concentration because the adsorption sites adsorbed the available chromium more quickly at low solute concentrations. However, for higher concentrations, intra-particle diffusion was predominant adsorption mechanism. The effect of pH on Cr(VI) removal was studied and found that the percent removal increases to maximum at pH 2.5 and thereafter decreasing sharply and continuously.

Patnaik & Das (1995) used blast furnace flue dust generated in the steel plants for the removal of hexavalent chromium. Results showed that at lower initial concentration of Cr(VI), the efficiency of removal of Cr(VI) is higher at lower pH. Similarly there is a definite decrease in percent removal from 16.3 to 10.1% with the increasing temperature from 301 to 323K. With the increase in adsorbent dose from 10 to 15 mg/l, Cr(VI) removal efficiency increases to more than 90% when the Cr(VI) concentration is in between 2 to 5 mg/l.

Singh, Saksena et al (1994) investigated the removal of Cr(VI) using leached acacia arabica bark which was treated with formaldehyde in acidic medium to prevent its colour leaching tendency. Sorption of Cr(VI) decreases with increase in pH (9.25mg/g at pH 2.0 to 2.5mg/g at pH 6.8). The equilibrium time was found to be 2.0 hrs. For complete removal of 50 mg/l of Cr(VI), adsorbent having a particle size of 0.44 & 1.22 mm was required in quantities of 3 and

10 mg/l respectively and the adsorption data followed the Langmuir isotherm.

Srivastava, Gupta, et al (1996) reported that the removal of lead and Chromium from waste water using activated carbon developed from fertilizer waste material. Authors stated that the removal of Cr (VI) was maximum at pH 2.0, where as in case of lead did not change much with increase in pH and 50-80% of the removal occurs within the first one hour contact time. The optimum parameters are found as (i) dose of adsorbent as 1.0g/l (ii) temperature 30°C (iii) particle size of 150-200 mesh (iv) adsorbate concentration of 1×10^{-2} M.

Srivastava, Gupta, et al (1997) used a activated blast furnace slag generated from steel plants for the removal of lead and chromium. Optimum pH for the removal of lead and chromium is 4.0 and 1.0 respectively. The effective temperature for both Cr and Pb is found as 30°C. Authors also conducted column studies and found that the maximum removal of Cr and Pb was obtained in a wide range of concentration using activated slag. It has been possible to quantitatively recover Pb by 1% HNO₃ and the product has been tested for the removal of metal ions from the effluent of a metal finishing plant. Authors concluded that the performance of activated slag as an adsorbent is comparable to commercially available activated carbons.

Srinivasan, Balasubramanian, et al.(1988) reported the removal of Cr(VI) by rice husk carbon and compared the results with commercial activated carbon. It was reported that 88% removal of total chromium and 99% removal of hexavalent chromium in the pH range of 2.0-3.0 with a carbon dose of 1.6gm/l and equilibrium time of 4 hrs.

Sharma Y.C (1996) studied the foundry material for the removal of Cr(VI). It was observed that the removal increased from 41.7 to 69.5% by decreasing the concentration of Cr(VI) 2.0×10^{-4} M to 0.5×10^{-4} M at 0.01 M NaClO₄ ionic strength, pH 2.5, temperature 30°C and a particle average size of 100 micro meter.

Sujata, Surendra Kumar, et al(1995) used the spent myrobalan nuts, a waste product for the removal of Cr(VI). It was found that 1.0 gm/l of spent nut removes 97% of Cr(VI) at optimum contact time of 75 minutes & pH of 2.5, for concentration of 5.0 mg/l.

Narayana and Krishnaiah (1989) studied the removal of chromium using bituminous coal. The amount of chromium adsorbed at different pH ranging from 1.0-6.0 was observed at different adsorbent doses varying from 0.5 -10 gm/l, and found that removal was maximum at pH 2.0. Also observed the percent reduction of Cr(VI) to Cr(III) was maximum (12-49%) at pH 1.0.

Periasamy , Srinivasan, et al (1991) investigated the removal of Cr(VI) by using activated groundnut husk carbon. Results showed that at pH 2.0 the Cr(VI) removal was 80%. Optimum dose of adsorbent for the maximum removal (100%) was 2400 mg/l when an initial Cr(VI) concentration was 10 mg/l. The adsorption capacities calculated by Freundlich isotherm gave 5.61 mg/g and 3.54 mg/g of Cr(VI) removal at pH 2.0 for distilled and tap water respectively.

Deepak & Gupta (1991) used activated carbon and alumina for the removal of Cr(VI). It was found that 5g of activated charcoal could reduce 100% Cr (VI) from a 200 ml sample containing 200 mg/l at natural pH. With increase in initial Cr (VI) concentration there was corresponding decrease in percent Cr (VI) removal, because of the limitations of surface area for adsorption. For the same concentration alumina (Al₂O₃) showed 58% removal when 5.0 g/200 ml. of adsorbent dose was given.

Samantaroy, Mohanty, et al.(1998) investigated the removal of Cr(VI) using Kendu fruit gum dust (KGD), drum stick gum dust (DGD) and green peas skin dust(GBSD). The results obtained are compared with the other adsorbents are presented in table no 1.1.

Table 1.1 Comparative studies of different adsorbents

Absorbent	Initial Cr (VI), mg/l	Eqbr. time, hr.	Dose gm/100 ml	pH	% Cr(VI) removal
Bagasse ash	10.0	3	6.0	2.0	53.4
Activated bagasse	10.0	1.5	1.0	0.85-2.0	99.97
Raw bagasse	10.0	1.5	1.0	1.0	93.5
Activated jute carbon	10.0	1.5	1.0	1.4-2.0	99.7
Activate charcoal	100.0	-	5.0	-	100
Fly ash	25	24	22	1.5-2.5	86
Calcinated coke	5.0	-	-	2.0	100
Activated GHC	10.0	3.0	0.24	2.0	80
Kendu fruit gum dust	6.0	6	0.1	6.1	100
Drum stick gum dust	2.5	5	0.3	6.9	100
Green peas skin dust	2.5	4	0.35	6.7	96

1.4 REMOVAL OF LEAD AND ZINC

Raji, Shubha, et al. (1997) worked on the removal of Pb (H)using chemically modified saw dust (SD) of rubber wood of size.-80+2.30. Two parts of this SD was treated with 20 parts of 0.2N H₂SO₄ and five parts of 39% HCHO and kept in hot air oven at 50 °C for 6 hours. This polymerized saw dust (BSD) was washed several times with distilled water and again dried at 60°C. Authors used batch adsorption process and removed Pb(n) from 21.22 mg/g, (85%) to 39.14 mg/g (78.4%) by increasing the adsorbate dose from 50 mg/l to 120 mg/l at a constant pH of 6.0. Regarding the effect of pH, experiments were conducted for varying pH between 2.0 to 9.0 and found that, lower the adsorbate dose more will be the percent removal. Secondly as the pH increases, the percent removal also increases to some extent and percent removal decreases even after increases in pH. The rearranged Langmuir equation,

$$Ce/q_e = 1/Q^0b + Ce/Q^0$$

Finally the authors have been concluded that the ability of BSD to adsorb Pb(n) from water depends on pH, initial concentration and temperature and the process obeys both Langmuir and Freundlich isotherms and is endothermic in nature. Hence the BSD may be effectively used as an adsorbent for the removal of Pb (II) from waste waters.

Vinod.K.Gupta, Dinesh Mohan etal (1998) used bagasse, fly ash, a sugar industry waste material for the removal of pb(II). Authors used batch adsorption studies to obtain the equilibrium data. Maximum removal of Pb(II) 50- 65% within the first hour of contact was obtained at pH 3.0, whereas at lower and higher pH, the percent removal was less. Further it was observed that, percent removal decreases with increase in temperature. The adsorption data obtained in the experimental work fitted to Freundlich and Langmuir adsorption isotherms. It was found that an adsorbent dose of 10 gm/l of size 150-200 mesh

removed 100% of Pb(II) at lower concentrations of adsorbate and 50-70% at higher concentrations. Rajasekhar, Sridharan, et al (1996) worked with fly ash for the removal of lead and zinc ions. Authors studied the effect of ion concentration on the retention characteristics of fly ash. It was observed that corresponding to maximum adsorption of 120 mg/gm, the minimum initial concentration of lead required to be 2900 mg/l. Similarly, maximum adsorption of zinc was observed (ie.19.1mg./gm) when the initial concentration of 920 mg/l. Another important factor studied was the contact time. It was found that at all the initial pH conditions 100 percent of retention was achieved at around 66 hours.

Bankar and Dara et al. (1985) investigated the use of febrifuga bark for the removal of lead. The optimum pH was found to be 4.0. Equilibrium time of 6 hrs required for maximum sorption of Pb(II) (98.42%), while 87.62% was adsorbed within 5 min. The amount of metal ion sorbed on the adsorbent decreased from 98.42% to 89.13% corresponding to 30°C and 90 °C. Further maximum sorption of Pb(II) occurred from acetate solution(99.16%) as compared to from nitrate solution(98.42%).It was also investigated the effect of light metal ions by adding 1 g substrate to the solution containing 89.25 mg/l of Pb and reduced the Pb from 98.42% to 88.8%, 80.39% and 73.95% in case of Na⁺, Mg²⁺ and Ca²⁺ respectively.

Gajghate, Saxena, et al. (1990) studied the adsorption of lead by activated carbon. The removal was maximum at pH 2.2 (100%), low at 5.5(94.5- 97%) and again increase at 6.0 (95-100%). It was concluded that coconut char based activated carbon can be used as an effective adsorbent. 0.75 ratio of carbon to lead removes 99.7% lead from 40 mg PbA solution after 5 hrs. of contact time and at pH 2.2. Desorption of lead (73%) can be achieved with HCl, whereas the desorption was less effective with NaOH & HNO₃.

1.5 REMOVAL OF CADMIUM

Sharma, Prasad, et al. (1991) investigated the removal of cadmium (II) on china clay. At pH 9.5, maximum removal (86.6%) and at pH 2.5 minimum removal (9.3%).of Cd(II) was found. Removal of Cd(II) was decreased from 80.3 to 51.3% by increasing the temperature from 30 to 50°C and equilibrium concentration occurred at a contact period of 80 minutes. The process of removal is exothermic hence low temperature is favorable.

Reed and Matsumoto (1993) examined the removal of cadmium by using two powdered activated carbons (PACs) in single and binary adsorbent systems. Two commercially available PACs, Darco HDB (American Norit Co.) and Nuchar SN (Westvaco Co.) were selected for the study. At low pH values, Nuchar SN removed more cadmium as compared to Darco HDB and at higher pH values the cadmium removal was opposite. Authors concluded that the surface complex formation (SCF) model successfully predicted the individual pH- adsorption edges when cadmium surface complexation constants determined from a parameter optimization procedure.

1.6 REMOVAL OF COPPER

Srinivasulu, Sundaram, et al (1998) used activated carbon generated sterculia foetida fruit (local name is

seema badam fruit) shell (SFFC) for the removal of copper(H) from aqueous solution. Seema badam fruitshell procured locally, dried at room temperature ground into small pieces, heated upto 573K in muffle furnace for 3 hrs. The carbonized material was washed with distilled water, dried and sieved into different mesh sizes. In their study, authors used three types of adsorbents such as water treated carbon(SFFC), acid treated carbon (ASFFC) and base treated carbon (BSFFC).Authors conducted the batch mode adsorption process and observed various parameters such as contact time, concentration of metal on pH, adsorbent dose, temperature for the removal of Cu(II). All the three adsorbents effectively removed Cu(D) between the pH range 6.1 to 7.6 and 4 gm/l of adsorbent dose, 293-323K temperature favored the maximum removal of Cu(II) ions.

Doultani, Rode, et al. (1999) investigated the removal of Cu(II) and Ni(II) from solution using eucalyptus globules bark substrate. The maximum removal was obtained at pH 8-10. It was found that 58% of Cu (II) and about 44% of Ni (II) ions were removed within 5 minutes. Sorbed metals can be leached out from the substrate using dilute nitric acid.

1.7 REMOVAL OF COLOUR AND COD

Sharma et al. (2008) studied removal of Methylene Blue dye from the effluents of textile industry using rice husk carbon activated by steam. The adsorbent was made from rice husk and was investigated under variable system parameters such as agitation time and dose of adsorbent. An amount of 0.08 g/l of RHAC could remove 10 to 99 % of the dye from an aqueous solution of 25 ppm with the agitation time increasing from 20 min to 200 min. The interactions were tested for both pseudo first - order and second - order kinetics and it was observed that the interactions could be better explained on the basis of first order kinetics.

Chatterjee et al. (2006) studied removal of Methylene Blue by chitosan hydrobeads. Adsorption process has been found to be dependent on temperature with optimum activity at 30°C. Both ionic interaction as well as physical forces is responsible for binding of Methylene Blue with chitosan.

Mittal et al. (2009) studied removal of Methylene Blue from wastewater using waste materials like bottom ash and deoiled soya and recovery by desorption. Column operations depicted good adsorptive tendencies for Methylene Blue with 96.95% and 97.14% saturation of dye on bottom ash and deoiled soya, respectively. Regeneration of the saturated columns has been made by eluting NaOH solution and more than 90% dye has been recovered in both cases.

Bhattacharyya et al. (2004) attempted removal of Methylene Blue from solutions using azadirachta indica leaf powder (neem leaf) as adsorbant. An amount of 0.6 g of the neem leaf powder (nlp) per litre could remove 52.0–99.0% of the dye from an aqueous solution with the agitation time increasing from 60 to 300 min. The results point to the effectiveness of the NEEM leaf powder as a biosorbent for removing dyes like Methylene Blue from water.

Kamel et al. (2009) decoloured Methylene Blue dye

solution by direct uv spectrophotometer at 254 nm and at pH 6.6 of the solution. It has been observed, that discoloration process of Methylene Blue solutions, became slow when concentration increased in the medium for the lowest concentration (10 ppm), about 70% of dye decolourization was reached after 7 h of irradiation.

Khadhraoui et al.(2009) investigated the degradation and mineralization of congo red, in aqueous solutions using ozone phytotoxicity and the inhibitory effects on the microbial activity of the raw and the ozonated solutions were also carried out with the aim of water reuse and environment protection. From his experiment he concluded that ozone by itself is strong enough to decolorize these aqueous solutions in the early stage of the oxidation process.

Mall and Upadhyay et al. (1998) used fly ash collected from paper mill and thermal power station for the removal of two basic dyes ie. methylene blue and malachite green from waste water It was reported that methylene blue and malachite green can be possible to remove to an extent of 97% and 88% respectively at an initial concentration of 20 mg/l with fly ash. Higher percentage removal obtained at higher pH, agitation speed below 150 rpm, contact time of 30 minutes and with 28-15 micron particle size. It was stated that the % removal increases with increase in temperature. Further reported that fly ash having less carbon content i.e. 5.57% is 96.7% efficient and fly ash with no carbon content is only 87% efficient.

Pragya Sharma, Amarjeet Kaur, et al.(1999) reported the adsorption capacity of five different low cost adsorbents for the removal of colour from the waste water containing malachite green. Experiments were conducted using saw dust, bagasse pith, orange peel, Eichhornia root and shoot collected from the vicinity of central pollution control board, New Delhi and compared the results with the activated carbon. These adsorbents were dried, grinded, sieved and then washed with 1% formaldehyde solution for overnight and washed well with distilled water. It was found that among the five adsorbents Eichhornia root was most efficient and removed 95-98% of the dye followed by Eichhornia shoot (92%), orange peel (95.6%), and saw dust (64.7%). Bagasse showed very less percentage of colour removal. Also the results showed that the removal of dye increases with increase in pH, which is 90-99% at alkaline range. This is mainly due to the excess hydrogen ion and binding of dye molecules on sorption site.

Pragya Tiwari and Shukla et al.(1999) reported the removal of reddish brown colour from distillery waste by using agro waste products i.e. wheat husk carbon (WHC), wheat stem carbon(WSC) and these results were compared by commercial activated

carbon(CAC) by Pragya Tiwari and Shukla. With an adsorbent dose of 6.0 gm/l @ pH 2.0, contact time of 2 hrs. , the colour reduction was 79.76,65.47 and 34.52% by CAC,WHC and WSC respectively. At pH 7.0 and adsorbent dose of 6.0 gm/l, the percentage colour removal was 52.38, 35.71 and go; 27.57 by CAC, WHC and WSC respectively. Freundlich's isotherm was developed for the reddish brown colour removal at pH2.0, adsorption and sorption period 120 minutes. The isotherm onto CAC and WHC indicate the uniform adsorption over the entire range of concentration.

Mall and Prasad et al.(1998) worked on low-cost effective effluent treatment of pulp and paper mill using pyrolysed bagasse char. Authors worked on the reduction of COD, colour using pyrolysed bagasse char and activated carbon at a constant temperature and a speed of 1560 rpm. It was reported that COD removal increases with increase in pH from 2-5 and then it starts decreasing with increase in pH. Similarly COD increases with increase in adsorbent dose of 15 gm/l thereafter there was no appreciable increase in COD reduction. It was observed that equilibrium time of 4 hrs and % removal was found to decrease with increase in initial COD concentration of 300 mg/l. At an initial COD concentration of 300 mg/l, the % reduction is 72% and 91% for pyrolysed bagasse char and activated carbon respectively at an adsorbent dose of 15 gm/l. Further it was seen that removal of colour to an extent of 64% and 80% by pyrolysed bagasse char and activated carbon respectively. If cost economics are considered, the cost of activated carbon is Rs.30,000/ton and pyrolysed bagasse char is of Rs.3000/ton only.

Kulkarni & Bal et al.(1986) reported the removal of colour by using granular activated carbon. Authors used four sizes of granular activated carbon (GAC) and observed various parameters which control the total adsorption Process. In all the cases four sizes of GAC, it was found that the equilibrium time was 6 hrs, the maximum percentage removal of colour was with particle size 1.18-2.36 mm and the test data follows both Langmuir and Freundlich isotherm. Authors also conducted the column tests for a flow rate of 9.55 ml/cm²/min. and concluded that by knowing the effluent quality, the optimum bed height and flow rate can be calculated.

Ramteke, Wate, et al.(1989) reported that the colour and organic matter from wastewater was successfully removed by using the pyrochar prepared from paper mill sludge. It was observed that at optimum pH of 4.0 to 5.0 and the results are presented in table no 1.2. Both colour and COD removal follows the Freundlich isotherm.

Table 1.2 Comparative removal of colour, COD & TOC by activated Carbons from distillery waste.

Sr	Activated Pyrochar				Granular Pyrochar				Commercial Char Coal			
	Dose, Gms/l	Colour, %	COD %	TOC %	Dose gms/l	Colour, %	COD %	TOC %	Dose gms/l	Colour, %	COD %	TOC %
1	1.0	43.5	37.9	6.19	2.0	39.0	33.3	10.52	0.5	57.5	38.6	15.0
2	2.0	51.0	40.0	25.23	4.0	48.5	46.5	23.68	0.7	66.6	48.5	16.5
3	3.0	-	-	-	6.0	54.0	73.3	31.05	0.9	72.5	50.6	26.05
4	4.0	72.5	46.6	33.33	8.0	61.5	-	33.94	1.1	73.5	53.3	26.31
5	5.0	78.0	-	-	10.0	75.5	78.6	38.94	1.3	81.0	55.3	25.52
6	6.0	82.5	54.6	30.19	15.0	83.0	86.7	52.89	1.5	86.0	50.0	26.05
7	8.0	92.0	65.3	42.4	-	-	-	-	2.0	92.5	52.0	33.68
8	10.0	98.0	64.0	42.9	-	-	-	-	-	-	-	-

Initial COD - 1168mg/l

Initial TOC - 380mg/l

Bokade, Thergaonkar, et al.(1990) reported the application of spoiled alumina, resulting from aluminum hydroxide manufacturing industry can be used as an adsorbent after activation at 400°C for 15 min. for the reduction of COD and colour from the paper mill and dairy industry waste water. The % removal of colour & COD (a) between pH 4-10 is constant (b) increases rapidly when dilution is increased up to 100 times. Authors stated that 99% colour removal & 84% COD reduction from black liquor, 64% COD reduction from dairy waste at the optimum dose of adsorbent 10 gm/l.

Ramaprasad, Pratapa Mouli, et al.(1985) investigated the ability of six low-cost adsorbent materials such as rice husk, bark, cotton waste, hair, coal and bentonite clay to adsorb basic, acidic, disperse and direct dyes from aqueous solutions. Bentonite clay has shown greatest adsorption capacity for majority of the dyes. Acid dyes are not adsorbed on most of the adsorbent materials. The absorbability of the basic red dye safranin was found to be higher on all the low cost materials as compared to basic blue methylene blue.

Gupta, Prasad, et al.(1991) reported removal of colour from dye-house waste water by using four low-cost adsorbents such as fly ash wollastonite coal and china clay. Equilibrium contact time was observed by varying the initial concentration of omega chrome fast blue at the optimized parameters for the maximum removal at pH, 3.5; temperature 30 ± 0.5°C; particle size 53 microns. It was found the adsorption capacity of different adsorbents in the order of fly ash > coal > wollastonite > china clay.

Namasivayam and Chandrasekharan et al.(1991) investigated the use Fe (ni) / Cr (in) sludge and red mud wastes can be used as adsorbent/ flocculent for removal colour from the waste resulting from dyeing industries.

Gupta, Prasad, et al. (1989) investigated the ability of china clay in the removal mordant blue-13, a popular dye. Equilibrium contact time was observed by varying the initial concentration of mordant blue-13, particle size and temperature at constant pH, 3-5 and temperature, 30±0.5°C. It was found that the equilibrium contact time as 160 min., initial dye concentration of 2.0 mg/dm⁻³ and particle size as 53 microns,

Gupta, Prasad, et al. (1988) studied the removal of Metamora chrome orange GL using fly ash. Time to reach the equilibrium was found to be 110 min. At pH of 3.0, initial dye concentration of 5 mg/l and the particle size of 48 cm x10⁻⁴, the % removal of Metamora chrome orange GL was found to be 98.45, 98.87 and 92.25 respectively.

1.8 REMOVAL OF ORGANIC AND OTHER PHENOLIC COMPOUNDS

Kannan.N and Karuppasamy (1998) used activated charcoal of tea powder and saw dust as an adsorbents for the removal of phenyl acetic acid(PAA) from the synthetic waste prepared of 0.2N PAA. The results were compared with the results obtained from commercial activated carbon at a constant temperature at 30 ± 1°C using batch adsorption technique, with a known concentration of PAA, varying the adsorbent dose between 5-100 mg/l, and contact time between 5-180 min. and obeyed the Freundlich isotherm. Authors conclude that used tea

powder can be used as an alternative adsorbent material to that of commercial AC for the low cost treatment of waste water containing organic acids.

Singh & Mishra (1990) reported that the removal of phenolic compounds by using treated saw dust. Authors used batch adsorption process with three types impregnated saw dust in Fe(III) form at a temp, of 25°C. Authors concluded that the maximum removal of phenolic compound was observed at a pH less than 3.0 and a flow rate of 2 ml/minute.

Mahadeva Swamy , Mall, et al.(1997) reported that the removal phenol by coal fly ash and activated carbon. Nearly 80% & 95% removal with coal fly ash and activated carbon respectively at an optimum pH of 6.5, adsorbent dose of 6.0 gm/l, temp. 30°C and a contact time of 90-120 min. Adsorption isotherms represented by Freundlich equation and indicate favorable adsorption with coal fly ash.

Srivastava, Gupta, et al.(1995) reported the removal of 2,4-dinitrophenol (DNP) using bagasse fly ash. It was observed that after 5.0 hrs. of equilibrium 92% DNP is removed by 15gm/l bagasse fly ash (particle size = 150-200 mesh, pH = 4.0, temperature = 30±1°C) whereas with 10.0 gm/l of the adsorbent, the removal is 86% under the same conditions. Material exhibits good sorption capacity and the data follows both Langmuir and Freundlich models. The cost cheapest variety of commercial activated carbon is Rs.10,000/ton, whereas the finished product of bagasse fly ash is Rs.400/ton including the cost of transport.

Mahadeva Swamy, Mall, et al.(1998) investigated the application of bagasse fly ash as an adsorbent for the removal of o- cresol and 81% was removed at an initial concentration of 100 mg/dm³. Adsorption process was confirmed to both Langmuir and Freundlich isotherm. Optimum parameters were derived and found the dose of adsorbent as 0.6 g, pH as 2.5 and contact time as 120 min for 80% removal.

Mahesh, Chitranshi, et al.(1998) reported the adsorption behavior of catechol on activated carbon. Results showed, maximum removal of catechol at pH 3.0 was 96.5% and 73.0% at pH 9.0. For simplicity in pH adjustment, it was considered as 5.0, various parameters optimized and found to be Temperature 30+/-2°C, adsorbent dose 12 gm/l, adsorbate concentration of 100 mg/l, contact time 2-3 hrs., particle size >2.0 and < 0.71 >1.4mm for the maximum removal of catechol. Freundlich isotherm model was applied to adsorption equilibrium data.

Ramu, Kannan, et al (1992) worked on the removal of carboxylic acids such as formic acid (FA), acetic acid (AA) and oxalic acid (OA) using fly ash and compared the results with activated carbon at 30°C. Optimum results for the removal of carboxylic acids are shown in table no1.3.

Table 1.3 Optimum conditions for the removal of carboxylic acids by adsorption on fly ash and activated carbon at 30°C. Initial concentration (Ci) = 0.2 g.eq./lit.

Condition	Fly ash			Activated carbon		
	FA	AA	OA	FA	AA	OA
Dose of adsorbent gm/l	8.0	7.5	10.0	2.2	2.0	2.5
Contact time min.	45	50	60	30	35	40
Percentage removal	85.0	82.5	86.0	98.0	95.5	92.5

Gupta, et al. (1988) studied the use of fly ash for the removal of chrome dye (met omega chrome orange GL). Authors reported that the optimum conditions for the maximum removal of chrome dye were found to be pH.4.5, Temp. 30°C, initial concentration 10mg/l. and equilibrium time 110 minutes. Kinetic data obtained from the studies have analyzed mathematically using the relationship between the contact time for the adsorption of the dye, t (minutes) and amount of dye adsorbed, q (mg/1).

$$\text{Log}(t+1) = kq^A$$

Where k and A are the empirical constants depending on initial dye concentration(Co) for a initial dye concentration of 5 mg/1, the relationship have been $\text{log}(t+1) = 0.411q^{1.002}$. Authors concluded that the mechanism involves an initial rapid rate of dye removal due to boundary layer adsorption followed by intra-particle diffusion which appears to be the rate governing step.

Gupta, Sharma, et al.(1998) reported that the use of bagasse fly ash as an adsorbent for the removal & recovery of phenol and p-Nitrophenol. The optimum parameters are (a) pH 4.0 (b) temperature 30°C(c) adsorbent dose 20 gm/1 (d) particle size 150-200 mesh. Adsorption data followed both Langmuir and Freundlich isotherm. Exhausted media can be chemically regenerated by 1M HNO₃. Akram and Youge (1992) studied the sorption onto activated carbon in fixed bed reactor for the removal of hazardous organics from water and wastewater. Authors reported that the present fixed bed reactor design procedures could be both expensive and time consuming. Mathematical process modeling could reduce the cost and time by decreasing laboratory and pilot scale experimentation. The use of semi discrete Galerkin finite element method (SDGFEM) with an asymmetric interpolating function was found to eliminate this special oscillation resulting in computationally efficient algorithm. The computational effort necessary is of order N. Additionally; the introduction of the asymmetric weight function eliminates special oscillation from becoming negative. Authors concluded that not only does the SDGFEM permit the use of simple integration routines to solve the discredited equations, it also results in a stable algorithm. Also reported that the model is sensitive to changes in the film-transfer co-efficient.

CONCLUDING REMARKS:

From the above literature study it is observed that biosorption is the most economical and eco-friendly method for removal of heavy metal from domestic as well as industrial wastewater. Low cost adsorbents in natural form add the lignin to the effluent and increase the BOD, which is to be treated again. To compensate this limitation the agro-waste or selected low cost adsorbent proves to be more efficient after modification. The problem arises regarding the disposal of exhausted adsorbent can be solved either by its activation or incineration or disposal after proper treatment.

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