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Research Papers

HARVESTING RAINWATER WITH A GROUP OF HOUSES TO RECHARGE GROUNDWATER RESERVOIR

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Abstract

Many places in the world face acute scarcity of fresh water in both terms of quantity and quality. The overexploitation of groundwater is a serious global problem. Rooftop rainwater harvesting (RRH) requires connecting the outlet pipe from the roof top to divert collected water to existing well, tube well, bore well or a specially designed well. Urban housing complexes and institutional buildings having large roof area or a group of residential buildings can be utilised for RRH. The Central Groundwater Board of India has suggested several methods of RRH for individual houses and multistory buildings only. We have designed RRH techniques for housing complexes that are useful for a group of residential buildings. Rainwater is the purest form of natural water. It can be used as recharge water without any treatment. The water used for aquifer recharge can be taken from any source but it must be pure like rainwater or drinking water. It should not have even soil, sand and silt in it. Recharge water should be surely silt free. Filters remove particulates. If germs are present in the collected rainwater, it should be UV irradiated or ozonized before using it as recharge water. Strict regulations regarding aquifer recharge are required. Harvest the rain. Wrangle water from the sky for watering, washing and even drinking by using a RRH system.

Keywords: Roof, rainwater, harvesting, houses

INTRODUCTION

Roof rainwater harvesting (RRH) is a process of capturing rainwater off a roof and storing it for future use. It is rainwater capture and storage for reuse as it falls onto a roof surface of a building (Standards Australia 2006). If used for drinking, roof materials must be compatible for contact with drinking water (Colorado Division of Water Resources 2009). Water harvested from a roof catchment can be improved in storage from a natural distillation process. Risk to water quality can be from airborne particles and from man-made air pollution. Rooftop catchment systems gather rainwater from the roofs of houses, schools, etc., using gutters and downpipes (made of local wood, bamboo, galvanized iron or PVC), and lead it to storage containers that range from simple pots to large ferrocement tanks. If properly designed, a foul-flush device or detachable downpipe can be fitted that allows the first litres of runoff from a storm to be diverted from the storage tanks. The runoff is generally contaminated with dust, leaves, insects and bird droppings (Rainwater Fact Sheet 2007). Sometimes the runoff is led through a small filter of gravel, sand and charcoal before entering the storage tank. Water may be abstracted from the storage tank by a tap, hand pump, or bucket-and-rope system (WHO et al. 2003).

RRH requires connecting the outlet pipe from the roof top to divert collected water to existing well, tube well, bore well or a specially designed well (TWDB 2005; WHO et al. 2003; CGWB 2000). Its components are catchment area (roof); conveyance system (guttering, downspouts, and piping); storage (cistern or tank); filtration and distribution. The storage tank can be as simple as directing gutters to a lidded garbage can or as complex as a concrete cistern, roof washer and filtration system (Camilli 2000). So it involves the main cost of the entire recharge system. Retrieving water from the tank can be done by gravity, if the tank is high enough, or by pumping, similar to the method used to withdraw and pressurize water from a well. Taking the process further, runoff could be collected and stored for use in the immediate facilities, thereby reducing city-supplied volumes, or for sending water back to the municipal facilities. If the infrastructure could be created or modified to direct runoff to city storage facilities, that water could be treated and added to the potable supply. Cities that currently have underground drainage systems might continue those systems to direct the flow to wherever they can store the high volumes associated with hard surface runoff (Vani et al. 1997). Urban housing complexes and institutional buildings having large roof area or a group of residential buildings can be used for RRH.

The Central Groundwater Board of India has suggested several methods of RRH for individual houses and multistory buildings (CGB 2000). The present study aims to depict RRH techniques for housing complexes that are useful for a group of residential buildings or a colony. RRH gives pure water at very low cost.

RAINWATER ENDOWMENT AND HARVESTING POTENTIAL

The total amount of water received as rainfall over an area is called the rainwater endowment of that area. Out of this, the amount that can be effectively harvested is called water harvesting potential.

$$\text{Water harvesting potential} = \text{Rainfall (mm)} \times \text{Collection efficiency}$$

Many factors affect collection efficiency. The amount of rain is the main factor. Three-hundredths to one-tenth of an inch of rain is needed to wet the roof and fill the roof washer, some of the rain overshoots the gutters or spill out of the gutters during heavy downpours. Other factors are capacity of storage tanks, runoff coefficient, the first flush wastage etc. Efficiency is usually presumed to be 75% to 90% depending on system design and capacity.

$$\text{Volume of rainfall over the rooftop} = \text{Area of rooftop} \times \text{Average annual rainfall} \times \text{Runoff coefficient}$$

WATER QUALITY

As rainwater may be contaminated, it is often not considered suitable for drinking without treatment. However, there are many examples of rainwater being used for all purposes — including drinking — following suitable treatment.

Rainwater harvested from roofs can contain animal and bird faeces, mosses and lichens, windblown dust, particulates from urban pollution, pesticides, and inorganic ions from the sea (Ca, Mg, Na, K, Cl, SO_4), and dissolved gases (CO_2, NO_x, SO_x) (Magyar et al., 2008). High levels of pesticide have been found in rainwater in Europe with the highest concentrations occurring in the first rain immediately after a dry spell. The concentration of these and other contaminants are reduced significantly by diverting the initial flow of water to waste as described above. The water may need to be analysed properly, and used in a way appropriate to its safety. In Brazil alum and chlorine is added to disinfect water before consumption. So-called "appropriate technology" methods, such as solar water disinfection, provide low-cost disinfection options for treatment of stored rainwater for drinking. Harvested rainwater can be boiled in parabolic solar cookers before being used for drinking.

DECONTAMINATION AND DISINFECTION

Rainwater is the purest form of natural water. It can be used for aquifer recharge without any treatment. The water used for this purpose can be taken from any source but it must be pure like drinking water or rainwater. It should not have even soil, sand and silt in it. Recharge water should surely be silt free. If germs are present, it should be UV irradiated, ozonized or chlorinated before using as recharge water.

There are many filtration methods and roof-wash systems for decontamination that vary according to intended use. One method uses a floating filter connected to a flexible water line inside the tank. This method withdraws water from approximately 30 cm below the surface, considered to be the cleanest water 30 cm in any body of water. The water to be used for human consumption can pass through an inline purification system or point-of-use water purification system such as an ultraviolet filter. Uses other than for human consumption do not require any purification.

Preliminary filtration and a roof-wash system provide the first line of defense against contamination. RH systems supplying potable water also should include measures to treat water before use (Hartsung 2002). Several treatment options including microfiltration, UV sterilization and ozonation, are available. Many experts agree that filtration and UV treatment provide adequate protection, making ozonation unnecessary.

Most systems use a combination of physical filters which remove particulates, and a UV-light chamber which kills bacteria and other organisms by exposing them to high-energy ultraviolet light.

A less expensive option is to treat water with chlorine or iodine, as is typically done with municipal water. The most common chemical added is chlorine in the form of sodium hypochlorite which is available in liquid form. Household bleach which is 5% sodium hypochlorite, is commonly used. Chlorination spoils the taste of the treated water and harms human health with harmful chemicals that could result from the added chlorine. In the presence of organic matter, chlorinated hydrocarbons may be formed which are suspected carcinogens.

ROOF WASHER

Between rainstorms, various pollutants can settle out of the air and onto the roof. Many RH systems incorporate a roof washer to keep these contaminants from entering the tank. Roof washers capture and discard the first several gallons of rainwater during a storm before conveying the rest to the tank. A very simple roof-wash system can be made out of a 15- or 20-cm vertical PVC or polyethylene pipe installed beneath the gutter with an inlet just above each downspout to the tank.

AWARENESS

Awareness campaign is essential for RRH (Anon 1998). It needs:

- ❖ Educational materials from government agencies, NGOs and the aqiufer communities
- ❖ Aquifer issues to be brought into primary and secondary school classrooms, and to environmental educators at museums, state parks, market places, and soil and water conservation districts.
- ❖ Numerous presentations and workshops
- ❖ Education to landowners, local government officials, utility managers, citizens groups, and the public about source water issues.
- ❖ Printed materials, TV documentaries and a website for wider dissemination about

MONITORING

Regular monitoring of rainwater, harvesting system particularly water in the storage tank and groundwater in the aquifer is required (Agarwal, 1998). The following points should be kept in mind:

- *Water parameters:* COD, bacteria, nitrate, fluoride, arsenic, heavy metals, pesticide and excess nutrients
- *Techniques:* Isotopic analysis, antibiotic resistance analysis and general water quality testing
- *Detailed evaluation:* The extent and land use of the recharge area, and surface and groundwater movement in the basin including mobility, persistence and distribution of toxics
- *Environmental compartments:* Water, soil, food, air and biota to obtain baseline values and trends over time
- *Data use:* Validating predictive models like Aquifer Vulnerability Assessment (AVA)

ROOF AS THE MOST COMMON RAINWATER CATCHMENT SYSTEM

The roof of a building is the most common rainwater catchment system, though a separate building designed especially for rainwater harvesting (a "water barn") may be used.

The best roofing material for rainwater catchment is uncoated stainless steel or factory-enameled galvanized steel with a baked-enamel, certified lead-free finish. With any metal coating, the manufacturer must be asked whether the coating contains heavy metals. Red paint used on metal often contained lead in the past. Any existing metal roof being used for a potable water catchment system should be tested for lead.

Wood shakes, concrete or clay tiles, and asphalt shingles are more likely than other materials to support the growth of mold, algae, bacteria and moss which can potentially contaminate water supplies. Treated wood shingles may leach toxic preservatives, and asphalt shingles may leach small amounts of petroleum compounds. In addition to the health concerns, a porous or rough roof surface holds back some of the water that would otherwise make it into the cistern. Asphalt roofing has a "collection efficiency" of about 85% while enameled steel has a collection efficiency of more than 95%. With asphalt roofing, more of the rainwater stays on the roof in a typical rainstorm (i.e., the roof stays wet), though the actual percentage depends on the duration of the storm.

To be most effective, the roof should be fully exposed and away from overhanging tree branches. This reduces the risk of contamination from rotting leaves or droppings from birds and insects in the trees. If possible, avoid using roofs of buildings that rely on wood heat, as the smoke particles and soot deposited on the roof may contain PAHs and other hazardous materials.

RRH METHODS FOR AQUIFER RECHARGE

RRH for an individual house or a group of houses requires connecting the outlet pipe from roof-top to divert collected water to existing well, tube well, bore well or a specially designed well (Hartsung 2002; Gould and Nissen-Petersen 1999). Rooftop rainwater collected may be used to recharge groundwater reservoir through any one of the following proven techniques:

1. Abandoned or Running Well

This method can be used for a colony provided hydrogeological parameters permit. For a group of houses the recharge well should be so deep that it can saturate water of the entire area.

2. Settlement Tank

It is used to remove silt and other impurities from rainwater. It can have an unpaved bottom surface to allow standing water to percolate into the soil. It has provision for inflow, outflow and overflow. It holds excess of water till it is soaked up by the recharge structure. Any container masonry or concrete or underground tank, old disused tanks may be used as settlement tanks.

3. Recharge Pit

Recharge pits are constructed for recharging shallow aquifers. 1 to 2 m wide and 2 to 3 m deep recharge pit is generally constructed. After excavation, the pit is refilled with boulders and pebbles at the bottom followed by gravel and then course sand at the top. The collected water from the rooftop is diverted to the pit through a drain pipe. Recharge water is filtered through the pit.

4. Soakaway

It is a bored hole of upto 15 cm in diameter, drilled in the ground to a depth of 6 to 10 m. It can be left unlined if the soil is stable and clayey. It is filled with filter matter like brickbats and is lined with PVC pipe to prevent collapse. A small sump is made at the top of the soakpit where the runoff can be retained before it infiltrates through the soakaway.

5. Recharge Trench

A recharge trench is constructed when permeable strata of adequate thickness is available at shallow depth. It is constructed across the land slope along the boundary walls. It may be 0.5 to 1 m wide, 1 to 1.5 m deep and 10 to 20 m long depending on the availability of land and roof-top area. It is filled with boulders at the bottom followed by pebbles and by course sand at the top. The collected water from the roof is diverted through the drain pipe to the trench. The trench should be periodically cleaned. The method is suitable for a building having the roof-top area of 200 to 300 m^2. For a much bigger area a bigger trench is required or several trenches may be required.

6. Recharge Shaft

A recharge shaft is dug manually or drilled by the reverse/direct rotary drilling method. Its diameter varies from 0.5 to 3 m depending on the availability of water to be recharged and its depth varies from 10-15 m below groundwater level. It is back filled with boulders, gravel and coarse sand. The bottom of the shaft should end in permeable strata, i.e., course sand. It should be constructed to 10 to 15 metres away from the buildings for their safety. It should be cleaned regularly by scraping the top sand layer and refilling it periodically. It is constructed where shallow aquifer occurs below clay layer.

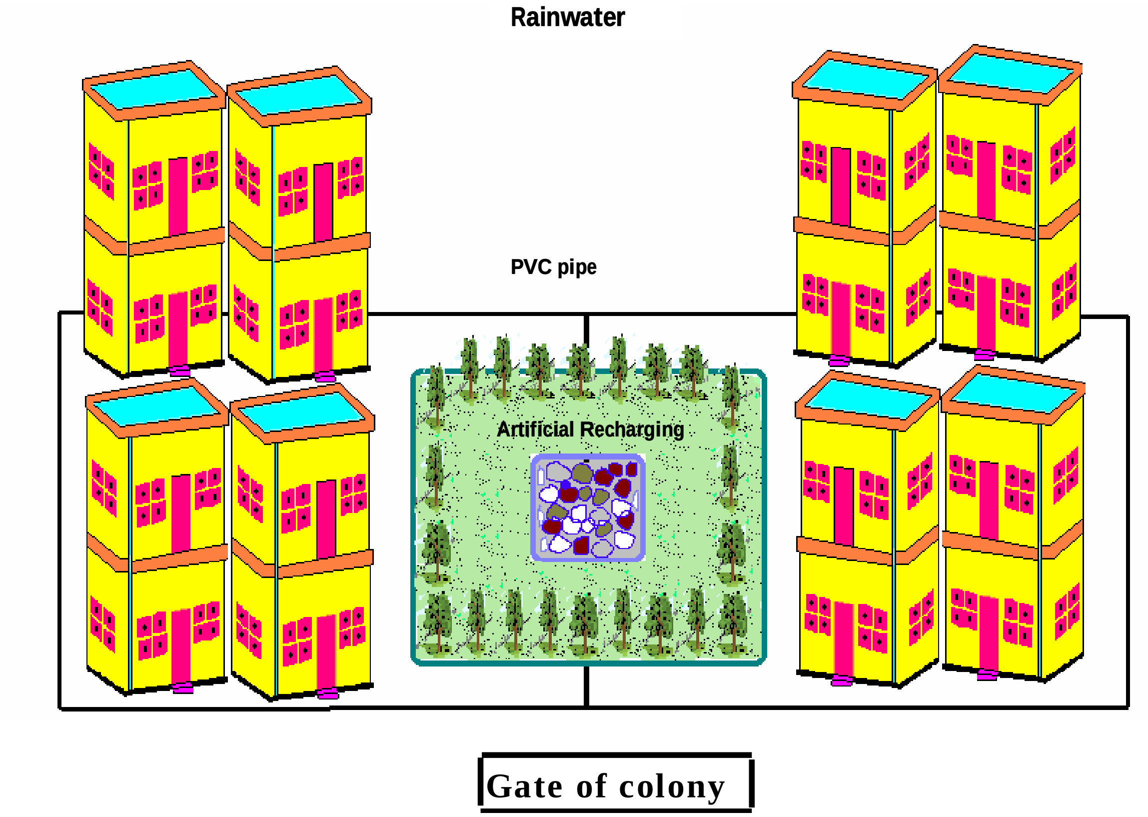

Figure 1. Recharge through borewell for a group of houses or a colony (Rainwater from the roof top is directed to the recharge borewell or pit in the centre of the park through PVC pipes)

7. Defunct Borewell

A defunct borewell can be used for recharging the aquifer under for a group of houses (Fig. 1). A circular pit of 1 m diameter for a depth of 0.6 m below ground level is dug around the borewell. The bore and the pit are filled with broken bricks. The top 0.3 m portion of the pit is filled with sand. The circular pit is covered with perforated slab at the top. The slab requires regular cleaning so as to keep its holes open to receive water.

BENEFITS OF RRH

Collecting and using rainwater has numerous benefits, ranging from improved water quality to reduced stress on underground aquifers (Table 1). RRH is a good option for aquifer recharge in urban areas where natural recharge is very low due to compaction, and not much land is available for implementing any other artificial recharge measure. Rainwater can be used for potable water (drinking, cooking, bathing) or nonpotable uses such as landscape irrigation, livestock watering and washing (Geerts and Raes 2009; Cluff 1981). Rainwater typically has very low hardness levels. High hardness reduces the use of soaps and detergents, and eliminates the need for a water softener. Fewer minerals also save wear and tear on plumbing fixtures. Stored rainwater also is a good standby in times of emergencies such as power outages or during periods of extreme drought when wells dry up; or where water supplies are not available, dependable or cheap. Rainwater harvesting reduces the impact on aquifers, lessening the demand on ecologically sensitive or threatened aquifers. Collecting some of the rainwater falling on impervious surfaces also minimizes erosion and flooding. Rainwater is pure. It is free from germs and organic matter, and is soft in nature. Because it doesn't have to be treated, pumped or distributed through a complex network, harvested rainwater saves energy and the use of chemicals. Some municipal water users sometimes switch to harvested rainwater as a way to avoid chlorination and fluoridation treatments. Rain runoff which otherwise flows into sewers and storm drains and is wasted, is harvested and utilised. RRH reduces strain on municipal water supply. It improves groundwater level, yield and quality. For example, the water level in the Panchsheel Park area, considered one of Delhi's posh colonies, was declining rapidly. Keeping in view the growing water problems, the Resident Welfare Association established a rainwater harvesting system for the entire colony, which improved groundwater level and quality.

Table 1. Assessment of quantity of rainwater harvested

	Individual Houses	**Multistoried building**	**Group of houses/Colony**
Roof top area	100 m^2	500 m^2	2500 m^2
Total quantity available for recharge per annum	50 m^3	250 m^3	1250 m^3
Water available for a 5- member family	100 days	500 days	2500 days

Direct capturing of rainwater significantly reduces our reliance and pressure on water sources such as rivers, dams, canals etc. It helps in reducing the flood hazard by improvement in infiltration and reduction in run-off. It improves groundwater quality through dilution, specially for hardness, fluoride and nitrate. It can reduce groundwater pollution by 80-90%. Rainwater may be harnessed at place of need and may be utilised at the time of need. The structures required for harvesting rainwater are simple, economical and eco-friendly.

LEGISLATION

Currently, there are no defined regulations regarding aquifer recharge in developing countries like India except RRH system is mandatory for new building constructions at some places, but certain rules do exist in developed nations such as USA (Colorado Division of Water Resources 2009). For example, Texas does not regulate rainwater collection for indoor or outdoor household use unless the system is backed up by publicly supplied waterlines. If there is a backup system, there must be an air gap between the public water lines and the rainwater lines. This air gap must exceed two diameters of the city line in width. The only other regulation regarding rainwater collection relates to physical maintenance of cisterns. This regulation is directed at public safety. To date, the primary governmental interest in rain and related runoff has been in pollution prevention. As more and more people begin to look to rain as a source of drinking water, the need for adequate regulation grows. The necessary regulations, whatever they may be, need to be started now while public implementation is still minimal. Legislations should seriously consider the following items: Distance from cistern to any source of contamination such as a septic tank, cistern height in relation to level of roof washer to ensure proper function, requirement of roof washer to capture the first flush, inclusion of overflow pipe directed to non-flooding area, sanitization minimum standards, filtration standards, application of drinking water standards to cisterns intended for potable supplies (regardless of number of people supplied), general health and quality standards for operation (prevention of mosquito breeding grounds), and structural standards to ensure proper design and installation.

SUGGESTIONS

Ensure the roof surface is of a suitable material for collecting quality rainwater. Analyze water samples from the storage tank to ensure If they are free from contaminants. Ensure the roof gutters are installed to building standards and have fall to outlets to prevent ponding and sludge build up. Install gutter mesh to prevent leaves and debris from blocking gutters and mosquito mesh to seal the storage from insects and vermin. Fit gutter outlets to underside of gutter to reduce sludge build up. Fit rain heads to down pipes to ensure the maximum discharge is delivered to the storage. Fit a first flush bypass system to separate debris and sludge before storage. Draw water from the aerobic zone in the storage. Ensure the roof catchment is maintained and cleaned on a regular basis.

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PHYTOREMEDIATION OF METALS

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Abstract

To study and report the ability of plants as biosorbents--For the first time biosorbent from plants waste have been demonstrated for efficient phyto- removal of heavy metals-Cd, Cr, Cu, Pb, Zn by plants such as canna, hibiscus, portulaca and trapa of which trapa fruit skin showed excellent results for metal binding capacity. The relevance of biomass was established for chromium menace in the tannery area at Zoyna International, Jajmau, Kanpur where the filter of Trapa adsorbent was installed for 15 days and shown that the adsorbent reduces- pH, conductivity, salinity and Cr(VI) considerably. In order to prove the utility of the metal adsorption from other industrial effluents we collected effluents from two scrap recovery plants – i) lead recovery and ii) zinc recovery. We used Trapa filter columns for the removal of Pb and Zn to demonstrate its utility. Thus we have shown that different plant wastes are suited for different metals. For example, Portulaca olecera has high zinc and Cr(VI) removal capacity. Canna indica has high cadmium and Cr(VI) removal capacity. Hibiscus rosa sinensis has high Zinc, Lead and Cr(VI) removal capacity used for Industrial effluents. Trapa exocarp has high Cr(VI) removal capacity and can reduce aqueous phase Cr(VI) up to non-detectable level used for tannery effluents.

The biomass grown in uncontaminated soils to adsorb or uptake lead, cadmium, arsenic, cobalt and copper from aqueous solutions, a working model was proposed for the industrial effluents. In order to help understand the metal binding mechanism, laboratory experiments we performed experiments to determine optimal binding pH, time dependency of binding, and binding capacity for each of the above mentioned metals. These experiments were carried out with crushed dry Portulaca stem mass and other plant material like dry biomass of Hibiscus and Canna flowers and Trapa fruit skin. Based on the efficacy of plant biosorbents, Trapa fruit skin was selected for further industrial effluent treatment. The effect of pH, contact time and adsorption equilibriums were investigated.

INTRODUCTION

The Initial objective of this study was to report the ability of portulaca, canna, hibiscus and trapa biomasses grown in uncontaminated soils to adsorb or uptake lead, cadmium, arsenic, cobalt and copper from aqueous solutions, a working model for the industrial effluents. In order to help understand the metal binding mechanism, laboratory experiments were performed to determine optimal binding pH, time dependency of binding, and binding capacity for each of the above mentioned metals.

Polluted Industrial areas of Jajmau, Kanpur, where most of the tanneries are located. Tezab Mill area in Kanpur is one such area where the ground water is very highly polluted with Cr-VI. There are other industrial effluents which have contamination of several heavy metals such as

Pb, Cd, Cu, As and many others. We first concentrated in chrome remediation, so as to establish the efficacy of the dried plant parts for metal removal.

The selected site of the affected areas are shown in Photo 1. The samples were collected from hand pumps where the industrial effluent has even affected the ground water aquifer.

Ground water condition of Cr(VI) in Sheikhpur Village, Jajmau

	Raw water collected	Raw water collected
Hand pump-I	10.442 mg/L	10.312 mg/L
Hand pump-II	3.834 mg/L	3.736 mg/L
Hand pump-III	2.945 mg/L	2.722 mg/L

Photo 1. Selected sites at the Kanpur Tannery area

Photo 2. Pumping station at Jajmau, untreated effluent used for irrigation

Photo 3. Nallah (drain) near a crop field at Jajmau

OBJECTIVES

- To investigate the effectiveness of Canna indica flower, Portulaca oleracea flower and stem Hibiscus rosa sinensis flower and Trapa natans fruit skin (exocarp) in the removal of various heavy metals from simulated wastewater under varying experimental conditions
- To establish the optimum conditions for maximum sorption by studying the effect of various operating variables

EXPERIMENTAL

Portulaca, hibiscus and canna flowers were collected from IIT Kanpur campus, dry biomass after dye extraction was prepared, trapa fruit skin after dye extraction was used for the study. De-ionized water (DI) water was used in all the experiments. The dye extracted materials were dried in oven at 90°C for one day, then the sample were ground using a mill and sieved to pass through a 100-mesh screen, particle size was determined for each biomass.

The study consisted of the following parameters:

a. pH profile study for Metal binding
b. Time Dependency Studies for Metal Binding
c. Metal Binding Capacity Studies

The laboratory methods used to determine the binding capacity of metals to the portulaca, canna trapa and hibiscus biomasses were carried out. For these experiments, 250 mg of biomass were taken. Two mL of 1ppm metal solution was added to each of the tubes and biomass- and were centrifuged. After centrifugation, the supernatants were saved for analysis and again 1 mL of 1ppm metal solution was added. This was repeated 3 times or until the saturation point was achieved and the final pH for all supernatants were recorded. Samples were diluted, as required to remain within the calibration linear range and metal concentrations were detected.

The experimental potential sorbents were Canna indica flower, Portulaca oleracea flower and stem, Hibiscus rosa sinensis flower and Trapa natans fruit skin (exocarp), which were being used in Facility for Ecological and Analytical Testing (FEAT) laboratory for exploring it's potential as natural dyes.

The remnant biomass of these plant parts after the extraction of natural dye were evaluated as sorbents for Cr (VI) and other heavy metals removal in dried. Exocarp of this fruit was used as potential biosorbent. Further investigations were carried out with sieved powders of all the plant materials as sorbents. Due to high sorptive capacity Trapa fruit skin (exocarp) dried and sieved powder was chosen for detailed sorption studies with hexavalent chromium while Portulaca, Hibiscus and Canna Dye waste were used for remediation of other heavy metals.

RESULTS AND DISCUSSION

A particle size analysis of the Trapa natans exocarp showed a d50 size corresponding to 148.49 um and a surface area of 0.68 m2/g; while Hibiscus flowers had d50 size 76.95 um and surface area of 0.78 m2/g. It has been reported that fine sized materials with a required reactive surface facilitate metal removal and pH neutralization.

In each set of the sorption experiments, there were 5-8 concentrations (from ~0.1 to 10 mM) and there were triplicate flasks for each concentration. After 24 h, 10 ml of the supernatant of the solution was collected for measuring the equilibrium (or final) metal concentration. The metal uptake by the sorbent was calculated using the following mass balance equation:

U = [(Q - Cf) x V]/m where U = metal uptake (mmol kg :); Q = initial metal concentration (mM); Cf = equilibrium metal concentration (mM); V = volume of the solution (l); and m = dry mass of sorbent (kg).

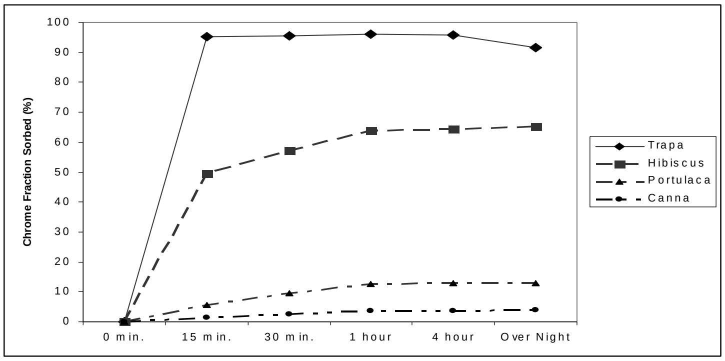

Figure 1. Sorption Kinetics of Cr(VI) for Trapa natans, Hibiscus, Portulaca and Canna

The remnant biomass of these plant parts after the extraction of natural dye were evaluated as sorbents for Cr (VI) removal in dried and semi- wet forms under static adsorption conditions(no agitation). Further investigations were carried out with sieved powders of all the plant materials as sorbents. Batch tests indicated that hexavalent chromium sorption capacity (qe) followed the sequence qe(Trapa) > qe(Hibiscus) > qe(Portulaca) > qe(Canna). Due to good sorptive capacity as shown in Figure 1, Trapa fruit skin (exocarp) and Hibiscus dye waste dried and sieved powder were chosen for detailed sorption studies.

Values of % uptake of 5 metal ions at equilibrium time by various Bio-sorbents have been shown in Fig. 2-7. Initial Concentration= 50 mg/l, Agitation Rate = 250 rpm, Temperature = 250C, pH = 6

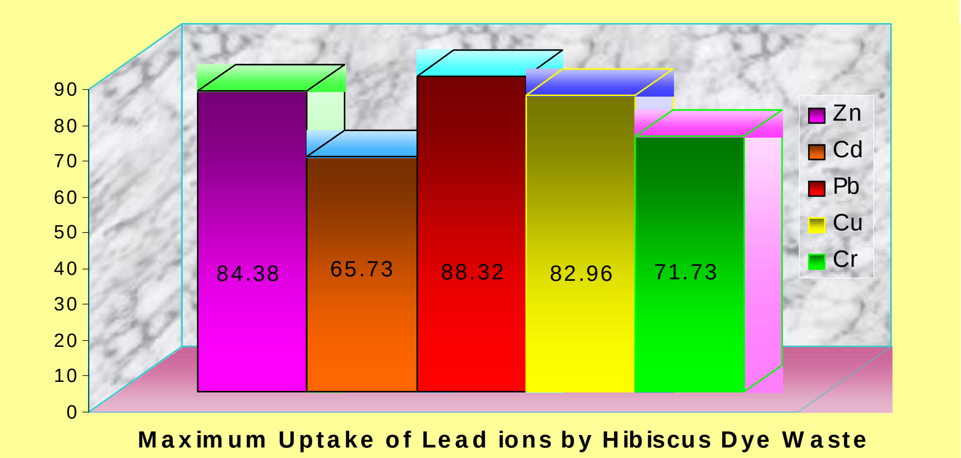

Figure 2. Metal uptake by Hibiscus dye waste

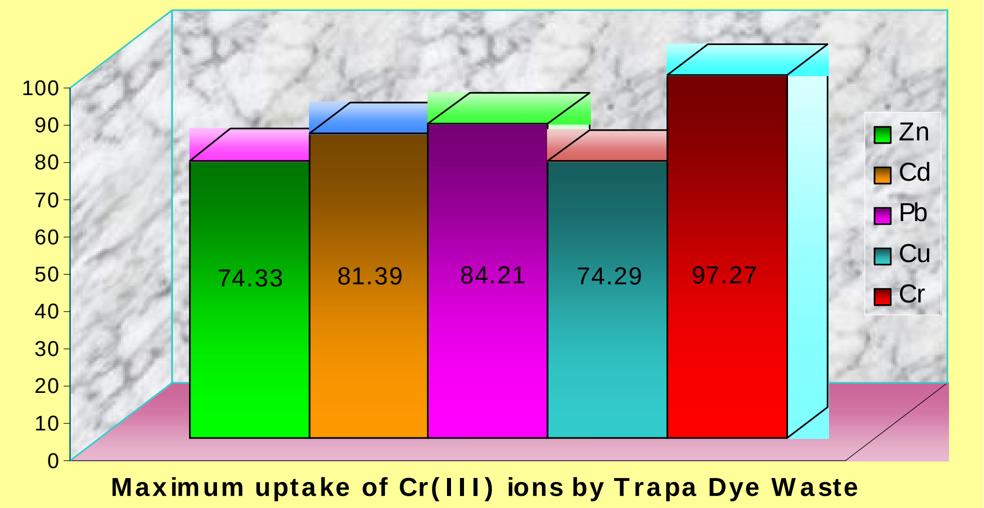

Figure 3. Metal uptake by Trapa dye waste

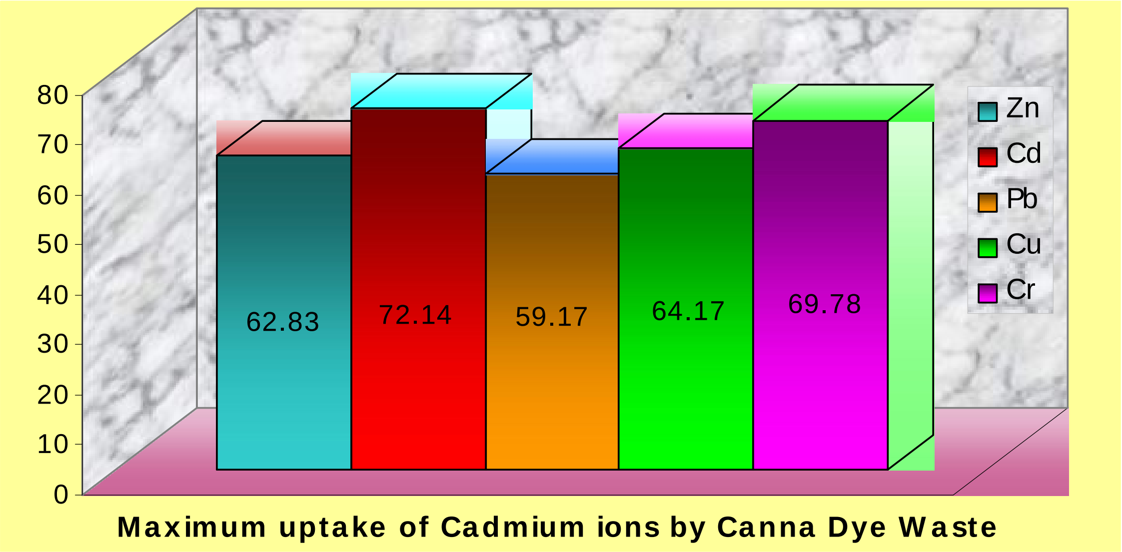

Figure 4. Metal uptake by Canna dye waste

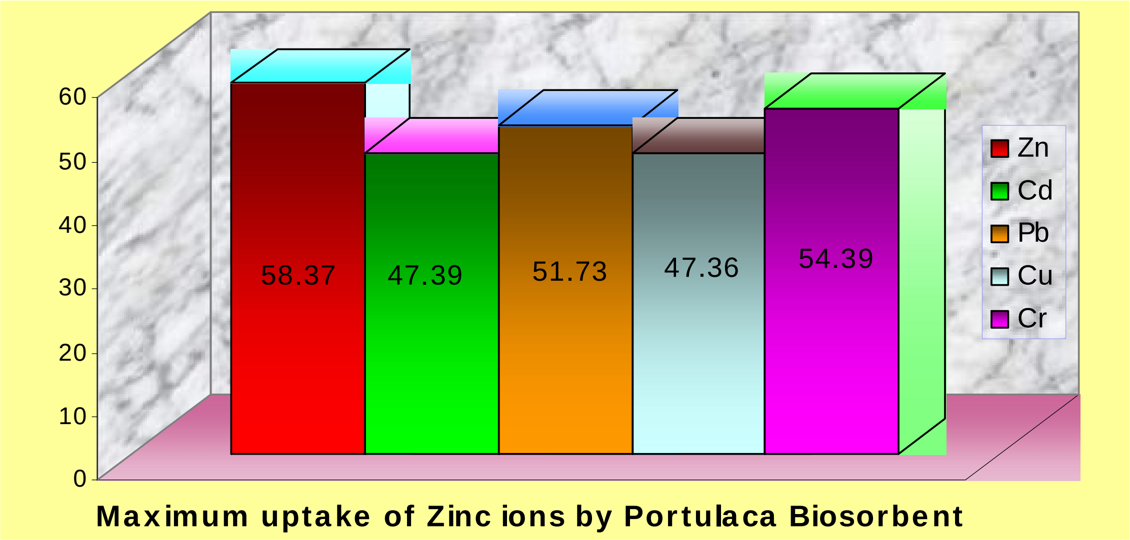

Figure 5. Metal uptake by Portulaca dye waste

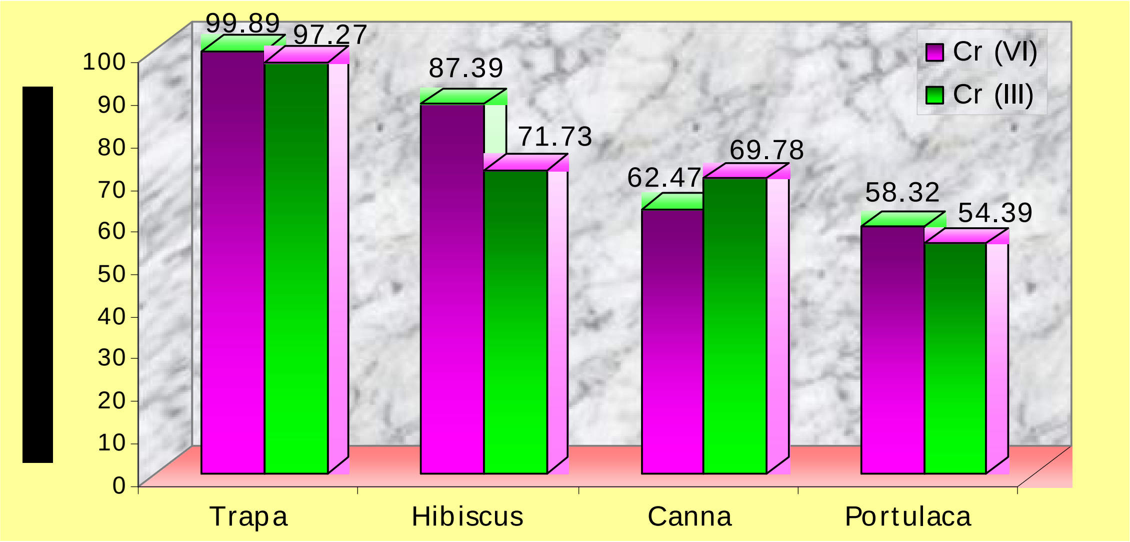

Fig. 6. Graphical representation of chromium uptake by 4 bio-sorbents at equilibrium time

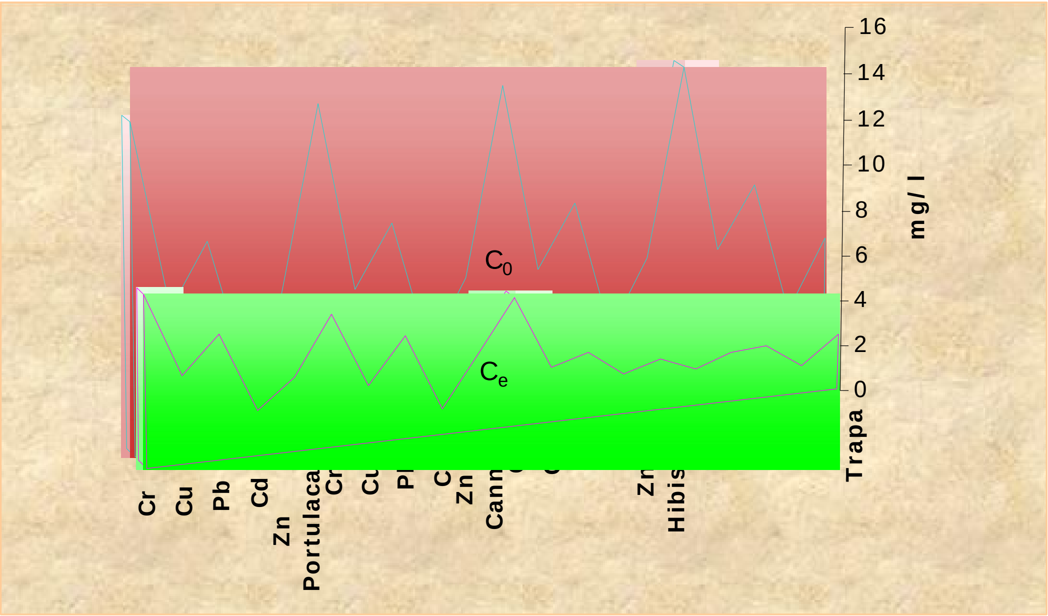

Figure 7. Remediation of tannery waste-water effluent with 4 bio-sorbents- Decrease in heavy metal concentration: Best results shown by Trapa dye waste bio-sorbent

Comparative data with other sorbent materials at industrial site and effective remediation have been given in Table 1 and 2.

Table1. Comparison of natural dye waste with known sorbents for remediation of Cr(VI) at pumping station point

	Raw water	Zeolite	Activated charcoal	Molecular sieves	Natural Dye waste
Pumping Station(Picture-2)	24.06 mg/L	7.37 mg/L	5.83 mg/L	6.12 mg/L	0.34 mg/L
Nallah near a crop field(Picture-3)	17.01 mg/L	4.77 mg/L	2.35 mg/L	3.98 mg/L	0.11 mg/L

Table 2. Comparison of natural dye waste with known sorbents for remediation of Cr(VI) for 5 ppm

Sorbent	pH	Time	Dosage	Percentage Reduction	Cost Effectivity
Activated Charcoal	pH 2	2 hours	10g/100ml	90.36 %	Rs 57 per 100L
Zeolite	pH 4	2 hours	10g/100ml	97.64 %	Rs 120 per 100L
Trapa fruit skin	pH 2-3	15 min	0.5g/100ml	99.74 %	Rs 5 per 100L
Hibiscus	pH 6	30 min	1.0g/100ml	98.12 %	Rs 7 per 100L

Demonstration of the Use of Filter

Filter with Trapa adsorbent was installed in Zoyna International Tannery, Jajmau for 15 days for the demonstration of the filter's efficiency. The filter was fitted in the effluent treatment plant of the tannery unit for 15 days and the raw water and treated water samples were collected every third day as shown in Table 3.

Table 3. Results of raw water and filtered tannery effluent

Sample/Day	pH	Conductivity mS/cm	TDS ppt	Salinity ppt	Cr (VI)
1/1(Raw)	7.61	2.148	1.088	0.811	0.633
1/2(Filt)	7.45	1.595	0.904	0.665	Nil
7/1(Raw)	7.66	2.167	1.268	0.921	0.768
7/2(Filt)	7.32	1.643	0.973	0.722	Nil
15/1(Raw)	7.53	2.059	1.064	0.818	0.752
15/2(Filt)	7.21	1.991	1.046	0.793	Nil

Photo 4. Filter fitted in tannery effluent outlet

Photo 5. Collection of filtered water

Table 3. Results of raw water and filtered lead scrap effluent

Sample/Day	pH	Conductivity mS/cm	TDS ppt	Salinity ppt	Pb content ppm	% Reduction
Raw water(Pb)	8.04	5.552	2.865	2.327	3.5	--
Filtered by Trapa DW	6.39	3.261	1.685	1.394	2.05	41.4%
Filtered by HDW	7.32	3.902	1.990	1.738	2.40	31.4%

Table 4. Results of raw water and filtered zinc scrap effluent

Sample/Day	pH	Conductivity mS/cm	TDS ppt	Salinity ppt	Zn ppm	% Reduction
Raw water (Zinc)	8.56	4.479	2.352	1.303s	1.236	
Filtered by Trapa DW	6.51	3.067	1.546	1.323	0.924	25.24 %
Filtered by HDW	7.56	3.183	1.643	1.525	0.153	87.6 %

CONCLUSIONS

Different plant wastes are suited for different metals. For example, Portulaca olecera has high zinc and Cr(VI) removal capacity. Canna indica has high cadmium and Cr(VI) removal capacity. Hibiscus rosa sinensis has high Zinc, Lead and Cr(VI) removal capacity used for Industrial effluents. Trapa exocarp has high Cr(VI) removal capacity and can reduce aqueous phase Cr(VI) up to non-detectable level used for tannery effluents.

FLUORIDE POLLUTION, TOXICITY AND PREVENTION

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Fluorine is the most highly reactive and chemically unstable of all elements. It is the 17th most abundant element in the earth's crust (Microsoft Encarta 2007). It is widely distributed in soil, earth and water as inorganic fluoride compounds, never in free state because of high chemical reactivity. It is a trace element essential for human life but is toxic at high concentrations. Virtually all rocks contain fluoride. It occurs naturally in the combined form as fluorite, cryolite and apatite. Most fluorine compounds are generally derived from fluorite (Wikipedia 2009). Fluorine also occurs as fluorides in sea water, rivers and mineral springs, in the stems of certain grasses, and in the bones and teeth of animals.

Fluoride (F^-) like other **halides**, is an anion i.e. monovalent ion with −1 charge. But as the lightest halide, its compounds often have properties that are distinctive. Both **organic** and **inorganic** compounds containing F^- are called fluorides and in many cases those containing covalent bonds to fluorine.

SOURCES OF FLUORIDE IN GROUNDWATE

Fluoride in groundwater is mainly due to leaching from fluoride bearing soils and rocks. Industrial sources are given in Table 1.

Table 1. Wastewater discharge standards for fluoride by CPCB (2000), India

Source	Standard in mg/l
General standards (aluminium, refrigeration, steel, rust removal, enamel, pottery plastic, glass, pharmaceutical, bricks, tooth paste, chemical industries, welding, automobile etc.)	2.0 (inland surface water) 15.0 (public sewers and coastal areas)
Phosphatic fertilizer	10.0
Complex fertilizer	10.0 (at fluoride removal outlet) 1.5 (at disposal point)
Oil drilling and gas extraction	1.5 (on-shore within 50 m) 2.0 (facility away from water body)
Petrochemicals (basic and intermediates)	15 (at fluoride removal outlet) < 5 (at disposal point)

OCCURRENCE OF FLUORIDE IN GROUNDWATER

A high fluoride content in groundwater has been reported from 25 countries (NIHFW 2007) like North and South American countries, India, China, Sri Lanka, Pakistan, Bangladesh, Argentina, United States of America, Morocco, Middle East countries, Japan, South African Countries, New Zealand, Thailand, West Indies, Spain, Holland, Italy, Norway, Mexico *etc.* In India, its occurrence in the upper aquifer system is endemic in 17 states such as UP, AP, Bihar, Gujarat, Rajasthan, Punjab, Haryana, TN, Karanataka, Kerala *etc.* Out of those 5 are hyper endemic, where 50-100% districts are affected viz. Andhra Pradesh, Tamil Nadu, Uttar Pradesh, Gujarat and Rajasthan. Fluorosis was first detected in India among the cattle by farmers of Nalgonda district, AP during early 1930's. Excess fluoride, wherever present in groundwater in India, is mainly in the concentration range of 1.5 to 6.5 mg/l against its desirable limit of 1 mg/l and maximum permissible limit (PL) of 1.5 mg/l in drinking water. **Fluoride value as high as 90 mg/l has been observed in Nagaur district of western Rajsthan and above 5.0 mg/l is quite frequent**. The groundwater in almost the entire Agra district is saline and has has excess fluoride that causes fluorosis((Gupta et al. 2008; Meenakshi and Maheshwari 2006; Gupta et al. 1994; Singh et al. 2000).

FLUORIDE TOXICITY

Excess fluoride in water causes dental fluorosis, skeletal fluorosis, thyroxine changes, kidney damage, respiratory disorder, fall in blood pressure, paralysis and system failure (Tabel 1). High fluoride inflicts plants also, and reduces productivity and biomass.

Table 1. Health impacts from long-term use of high fluoride concentration in drinking water (WHO 2004; NHMRC and ARMCANZ 2004)

Exposure dose, mg/l	Disorder
< 0.5	Dental caries
0.5–1.0	Promotes dental health
1.0-2.0	Dental fluorosis
3.0-6.0	Skeletal fluorosis (SF)
7.0-10.0	Crippling SF
>10	System failure

Fluorosis is desease without cure but it is a preventable crippling disease. > 90 million people suffer in China and India.

Several factors such as the age of the person, diet, health, vitamin and mineral deficiencies, genetic disposition, ethnicity, length of exposure, previous exposure to neurotoxicants, medications and environmental factors affect toxicity. Not all people react the same. **Age, sex, calcium intake in the diet, dose and duration of fluoride intake and renal efficiency in fluoride handling are the main factors which influence the outcome** (Dhaar and Robbani 2008)**.** Serum parameters rarely help in the diagnosis. **Elevated urinary fluoride and increased bone fluoride content are indicators of fluoride toxicity** (Maguire et al. 2007)**. Industrial fluorosis is on the increase on a global basis. Bone density measurement is a tool for early diagnosis.**

High fluoride inflicts several physiological and biochemical disorders in plants such as it inhibits germination, reduces photosynthetic ability, alters membrane permeability, causes ultrastructural malformations like injury in leaf tips and margins, reduces productivity and biomass.

Dental fluorosis (DF) is *mottling of teeth.* It is *tooth staining and brittleness* (Ismail and Hasson 2008). It is an aesthetic and social problem besides being a health problem. DF is a cosmetic effect that ranges in appearance from scarcely discernible to a marked staining or pitting of the teeth in severe forms. The teeth can be classified as normal, questionable, very mild, mild, moderate and severe (Photo 1).

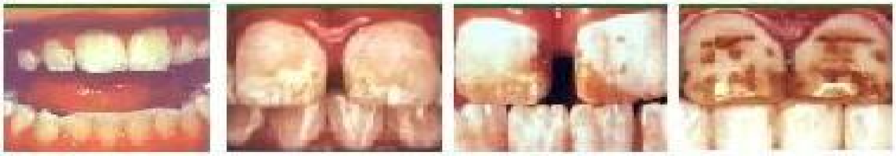

Photo1. **Very mild** **Mild** **Moderate** **Severe**

The discoloration of calcium rich constituents of teeth, viz., enamel and dentin may change the colour from white, yellow brown to black. The discoloration may be in streaks invariably horizontal in orientation, as during **development new layers of the enamel matrix are added in horizontal lines or bands on the teeth surface and never as vertical bands.** The discoloration may also appear as spots, but it is always away from the gums and on the enamel surfaces **and it can never be removed as it is an integral part of tooth matrix.** Fluoride combines with calcium during the mineralisation of teeth forming calcium fluoro-apatite crystals. DF is caused by an elevated fluoride level in or adjacent to the developing enamel. Thus, it follows that DF can develop in children but not in adults (Burt et al. 2003; Aminabadi et al. 2007). DF in an adult is a result of high fluoride exposure when the adult was a child or adolescent. For the studies on the problems involved in measuring the incidence and severity of DF **adequately trained individuals are required.** Teeth commonly affected are 1) central incisors 2) lateral incisors and 3) molars of the permanent dentition. **Fluorosis affects both the inner and outer surfaces of teeth, and can occur both in milk teeth and permanent teeth.** Teeth affected by fluorosis being poorly calcified (hypo-mineralised) loose enamel under the normal masticatory stress. Enamel has no regenerative capacity. Once it is lost, it is lost forever. The dentin is then exposed. A cavity formed in dentin spreads much faster and involves the pulp easily, leading to loss of teeth. The teeth once affected by DF cannot be reverted to normal, but the disclosed teeth can be masked by bleaching and /or by other methods. DF is prevalent in children who are born and brought up in an endemic area for fluorosis. It is one of the most widespread of endemic health problems associated with natural geochemistry. Endemic fluorosis is now known to be global in scope, occurring on all continents and affecting many millions of people. Although no precise figures for global sufferers exist, some figures at national levels have been given in the literature. In India and China alone, over 90 million may be affected, and when other populations in the Africa and the eastern Mediterranean in particular are taken into account, the global total may exceed 100 million. The dental effects of fluorosis develop much earlier than the skeletal effects in people exposed to large amounts of fluoride.

Clinical DF is characterized by staining and pitting of the teeth. In more severe cases all the enamel may be damaged. However, fluoride may not be the only cause of dental enamel defects. **Enamel opacities similar to dental fluorosis are associated with other conditions such as malnutrition with deficiency of vitamins D and A or a low protein-energy diet** (Mehrotra et al. 2007; Guney et al. 2007)**.** Ingestion of fluoride after six years of age will not cause dental fluorosis.

DF, which is characterized by discoloured, blackened, mottled or chalky-white teeth, is a clear indication of overexposure to fluoride during childhood when the teeth are developing. These effects are not apparent if the teeth are already fully grown prior to the fluoride overexposure. Therefore, the fact that **an adult may show no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit.**

DF is visible as soon as the secondary teeth erupt. While developing social and early life skills, children are at their most vulnerable to the psychological impact of discrimination.

Children who develop DF-related behavioural problems are more likely to be disruptive in school, underachieve, academically, regularly truant from school, have histories of antisocial behaviour or police records, and become drug and/or alcohol abusers. Many of these children carry these negative behavioural traits into adulthood and are more likely to live on welfare benefits, fail to obtain or retain work, become homeless, fail to make or maintain relationships, be more prone to violence, spend time in prison, become repeat offenders, suffer from some form of mental illness, suffer from drug addiction/alcoholism, have suffered from child abuse, and are child abusers. People with dirty or stained teeth have a lack of social skills, lower intelligence and poor psychological adjustment (Tang et al. 2008; Xiang et al. 2003).

Chronic high-level exposure to fluoride can lead to skeletal fluorosis (SF). It is a **crippling** bone disease of bone brittleness. It is characterized by loss of weight, anorexia, anaemia, wasting and cachexia. In SF, fluoride accumulates in the bone progressively over many years. The early symptoms of SF, include stiffness and pain in the joints. In severe cases, the bone structure may change and ligaments may calcify, with resulting impairment of muscles and pain.

Photo 2

Photo 3

The boy in Photo 2 has knees locked together and hones grossly deformed by fluoride in drinking goundwater**. Bending and weak legs signify skeletal fluorosis.** The girl in Photo 3 looks nine years old. She is 14. She cannot walk to school because her legs are cruelly bowed by fluorosis.

Acute high-level exposure to fluoride causes immediate effects of abdominal pain, excessive saliva, nausea and vomiting. Seizures and muscle spasms may also occur (Guney et al. 2007).

SF is not easily recognisable until the disease has developed to an advanced stage. In its extreme form, it currently affects millions of people living in India, China, and other poorer countries where nutritional deficiencies e.g. lack of calcium, exacerbate toxic effects of fluoride. Skeletal fluorosis comes in varying degrees of severity depending on nutritional status and level of exposure. Excessive quantities of fluoride when deposited in the skeleton is more in cancellous bone compared to cortical bone. Change in the bone is then revealed through radiographs. Maximum ill effects of fluoride are detected in the neck, spine, knee, pelvic and shoulder joints. It also affects small joints of the hands and feet. The usual complaints of the patients are pain in the neck, back, joints and rigidity begins in regions where cancellous bones predominates. With increased severity of skeletal fluorosis, pain is associated with rigidity and restricted movement of cervical and lumber spine, knee and pelvic joints as well as shoulder joints. Fluoride accumulates in the skeleton and the level of fluoride in the bone is determined by the dose (mg/kg of body weight/day), the duration of exposure, fluoride retention and other factors. In general, **the best predictor of the effects of fluoride upon the skeleton are the level of fluoride in bone, usually measured as the fluoride level in bone ash.** Beginning at a fluoride bone-ash level of about 6,000 mg/kg, stiffness or pains in the joints may be seen. At levels of about 7,500 mg/kg and above, chronic joint pain, calcification of ligaments and adverse effects may develop. In severe cases, depending on the bone-ash level and the individual, **muscle wasting and nerve damage** may occur.

Low amount of fluoride (0.3-1.0 mg/l) in drinking water is helpful in the prevention of dental caries and in treatment of osteoporosis. However, high intake of fluoride (>1.5 mg/l) in drinking water for a prolonged period is known to cause damage to the teeth enamel and eventually leads to skeletal complications that result in fluorosis: dental, skeletal and non-skeletal or combination of these. Fluoride is also known to induce ageing and no amount of medicine can cure or improve the damage.

Fluorosis is prevalent in many parts of the world and is caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride laden coal. Worldwide, such instances of industrial fluorosis are on the rise. Inhaling fluoride dust and fumes from industries is as dangerous as consuming fluoride containing food, water or drugs. Industrial fluorosis is a serious problem in the developed western and other industrialised countries. However, in India, the problem of industrial fluorosis is also reaching an alarming state due to rapid industrialisation.

It is well recognised that **consuming fluoride contaminated food or water for a period of 6 months to 1 year is adequate to have ill effects on the health.** Fluorine ingestion from all sources below 2.75 mg/day in adults leads to dental caries while above 7.75 mg/day results in various types of fluorosis. The prolonged use of drugs containing sodium fluoride is known to cause skeletal fluorosis.

FLUORIDE FACTS AND LETHAL DOSES (Yeung 2008; ADA 2005)

- **The total daily fluoride intake from all sources should not exceed 0.05-0.07 mg F / kg body weight in order to minimize the risk of dental fluorosis.**
- **The current sources of fluoride are tooth paste, infant formula, processed cereals, juice, soda, tea, wine, beer, mechanically deboned chicken, fish and sea food, teflon pans, fluoridated salt, fluoridated tap water, anaesthetics (enflurane, isofluran and sevoflurane), cigarettes *etc.***
- Prolonged exposure to 10 - 20 mg fluoride/person/day for 10 - 20 years can lead to crippling skeletal fluorosis in which osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity result.
- Approximately 1,200 mg (1.2 grams) of sodium fluoride ("just a pinch") can kill an adult human being. Approximately 200 mg can kill a small child.
- In the fluoridation process at the water treatment plant, fluoride is added to our water supply at the rate of 1 mg/l.
- Fluoride cannot be removed from drinking water with a charcoal filter, only a reverse osmosis filter or steam distilling process can remove fluoride. Boiling water for soup, coffee, tea or other drink, only concentrates fluoride.

- 20 billion lethal doses of fluoride per year, dumped into our environment through fluoridation.

REVISION OF FLUORIDE STANDARD

Water is a major source of fluoride intake. The 1984 WHO guidelines suggested that in areas with a warm climate, the optimal fluoride concentration in drinking water should remain below 1 mg/l (1ppm or part per million), while in cooler climates it could go up to 1.2 mg/l. The differentiation derives from the fact that we perspire more in hot weather and consequently drink more water. The guideline value (permissible upper limit) for fluoride in drinking water was set at 1.5 mg/l, considered a threshold where the benefit of resistance to tooth decay did not yet shade into a significant risk of dental fluorosis. **The WHO guideline value (WHO 2004) for fluoride in water is not universal. India, for example, lowered its permissible upper limit from 1.5 ppm to 1.0 ppm in 1998 (CPCB 2000).**

Dental fluorosis was observed in school going children and it declined after desilting of the tank. It was observed in the children even when water had fluoride content well within the permissible limits. Contrary to this, a family in northern Tanzania had been using groundwater containing fluoride of 10-14 mg/l for several generations without any harmful effects. Hence, **revision of fluoride standard is necessary in India.** This is because the effect of fluorosis is not associated only with high concentration of fluoride in water alone, but also its content in food, dietary habits, nutritional status, physical activity and body size of an individual. The revision of the fluoride standard should be based on atmospheric temperature and food habits. **Instead of having one standard for the entire country, it is better to have different standards depending on the area.**

PREVENTION

Fluorosis can be prevented or minimized by using alternative water sources, by removing excessive fluoride from drinking water and by improving the nutritional status of population at risk (Bruvo et al. 2008; Meenakshi and Maheshwari 2006; Kumar and Gopal 2000)**.**

Drinking water is the major source of fluoride for our body. Only good water (0.5-1.0 mg fluoride/L) should be used for beverage preparation. Children who consumed milk have a reduced fluoride intake. Tea is also a rich source of fluoride.

Ways to Remove Fluoride from Water

1. **Reverse osmosis filtration:** This is used to purify several types of bottled water (not all), so some bottled waters are unfluoridated. Reverse osmosis systems are generally very expensive.
2. **Activated alumina defluoridation filter:** These filters are used in locales where fluorosis is prevalent. They are relatively expensive and require frequent replacement, but do offer an option for home water filtration.
3. **Distillation filtration:** Commercially available distillation filters can be purchased to remove fluoride from water. When looking at bottled water, keep in mind that 'distilled water' does not imply that a product is suitable for drinking water and other undesirable impurities may be present.

These Do NOT Remove Fluoride

1. **Most common filters:** Some websites about fluoride removal state otherwise, but the product descriptions on the companies' websites confirm that fluoride is left in the purified water.
2. **Boiling water:** This will concentrate the fluoride rather than reduce it.
3. **Freezing water:** Freezing water does not affect the concentration of fluoride.

Steps to Reduce Fluoride Exposure

1. Don't take fluoride supplements.
2. Consider using unfluoridated toothpaste.
3. Avoid drinking black tea.
4. Black tea usually contains high amounts of fluorine.
5. Be wary of tinned fish and canned food items.
6. Avoid a preservative with fluoride.
7. Avoid black or red rock salt or items containing black or red rock salt.
8. Avoid using chewing tobacco.
9. Avoid long term use of medication that contains fluorine.
   Certain antidepressants and medications for osteoporosis contain fluorine.

Better Nutrition

Clinical data indicate that adequate calcium intake is clearly associated with a reduced risk of dental fluorosis (Warren and Levy 2003).. Vitamin C may also safeguard against the risk.The only practical and effective public health measure for the prevention and control of dental caries is the limitation of the fluoride content of drinking water to < 1.0 ppm and adequate calcium nutrition (dietary calcium > 1 g/day).

GENERAL ADVICE

Perhaps the best general advice that can be given in relation to local conditions is that, at a minimum, the fluoride level in local water supplies should be monitored and the population examined for signs of excessive fluoride exposure e.g. moderate and/or severe dental fluorosis and crippling skeletal fluorosis. Laboratory methods for fluoride determination, based on fluoride ion specific electrodes or colorimetric methods or even test kits, can be used for measuring fluoride concentrations but it is preferable to have on-line monitoring of the fluoride concentration using a continuous instrument.

A Final Word

Awareness should be created to use defluoridated water where there is a problem. Policy makers, scientists, doctors, public health engineers and NGOs should be involved in finding suitable methods to control fluoride pollution in general and fluorosis in particular.

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USE OF PYROAURITE TYPE SORBENT, ACTIVATED CARBON AND FLYASH IN REDUCING COD OF DOMESTIC WASTEWATER

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Abstract

The main components of domestic wastewater are proteins, carbohydrates, detergents, tannins, lignin, humic acid, fulvic acid, melanic acid and many other dissolved organic compounds that cause high values of chemical oxygen demand (COD). The aim of the research was to evaluate the ability of a synthesized pyroaurite type sorbent (PTS) as an alternative media over activated carbon (AC) and flyash (FA) for water treatment. Batch tests were carried out to reduce COD at different initial COD values, treatment times, adsorbent doses and pH values of the media. The results have indicated that the COD can be reduced upto the extent of 90 % by PTS or AC while use of flyash reduce COD upto about 60 %. The trend of COD removal % by PTS is fairly comparable to that of commercial activated carbon. Though the capacity of FA is lower than that of PTS or AC, the low material cost makes it an attractive option for the treatment of domestic wastewater. Thus, the treatment of domestic wastewater can be done not only PTS or AC but also by by flyash generated from thermal power plant or any factory to reduce the organic load.

INTRODUCTION

Pollution of water by organic and inorganic chemicals is of serious environmental concern. Domestic wastewater differs in characteristics from the industrial wastewater. In domestic wastewater the organic load mainly due to the processes like food processing, washing of floor, cloths, utensils, animals, bathing and sewage. The main components of domestic wastewater are proteins, carbohydrates, detergents, tannins, lignin, humic acid, fulvic acid, melanic acid and many other dissolved organic compounds (Manka et al. 1974). The organic content of wastewater is traditionally measured using lumped parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC).

Commercial activated carbon is regarded as the most effective material for controlling the organic load. However due to its high cost and about 10-15 % loss during regeneration, unconventional adsorbents like flyash, peat, lignite, bagasse pith, wood, saw dust etc. have been widely investigated for the removal of refractory materials (Pandey et al. 1985) for varying degree of success. Several investigations (Mott and Weber 1992; Viraraghavan and Dronamraju 1992) explored the use of flyash as an adsorbent for the treatment of wastewater to remove a variety of organic compounds and color. Gupta et al. (1990) used flyash for the removal of chrome dye from aqueous solutions and found that the mixture of flyash and coal (1:1) may substitute the activated carbon. Each of them concluded that flyash has a significant capacity for adsorption of organic compounds from aqueous solutions. It was reported that (Banerjee et al. 1995) the carbon content of flyash plays a significant role during the adsorption of organic compounds by flyash. The adsorption capacity increases with the increasing carbon content of flyash. However, a review of the literature showed that very little investigation has been conducted to find out the suitability of synthetic sorbent like PTS or flyash for the removal of COD from the domestic wastewater. The aim of the research was to evaluate the ability of a synthesized pyroaurite type sorbent (PTS) as an alternative media over activated carbon (AC) and flyash (FA) for water treatment.

IMPORTANCE OF THE STUDY

The research is likely to lead to the commercial development and modification of self synthesized pyroaurite type sorbent for water treatment having the following benefits: Al free, multipurpose, low cost and rapid sorption medium.

TOXICITY OF ALUMINIUM

Recently, aluminium exposure is hypothesized as a risk factor for development or acceleration of the onset of neuro-degenerative disorders as Alzheimer disease and encephalopathia in humans. The so-called biologically inert Al has cumulative effect and it has been reported to cause dementia (Lopez et al. 2000). It can cause brain damage, bone disease and anaemia in patients subjected to haemodialysis using water containing 0.1-1 ppm Al, which is the normal dose of Al (DL = 0.03 mg/l and MPL = 0.20 ppm) in drinking water where alum is used in water treatment plants. It is, therefore, required to explore and/or develop lower risk agents with no Al for humans with high performance in the water treatment.

REASON FOR SYNTHESIZING PYROAURITE TYPE SORBENT

Conventional sorbents face from different shortcomings:

1. Activated carbon is an ideal adsorbent for organics but has high production and regeneration cost.
2. Flyash has a significant capacity for adsorption of organic compounds from aqueous solutions. The carbon content of flyash plays a significant role during the adsorption of organic compounds. Flyash has a low sorption capacity and can not be used directly in column without modification.
3. Conventional sorbents can not remove contaminants rapidly from very dilute solutions (Kŏcí et al. 2004).
4. The use of microbes for water treatment is an attractive technique but unsuitable forapplications on a large scale.
5. The advanced treatment processes such as ion exchange, reverse osmosis, membrane separation, electrodialysis, chemical precipitation are very expensive.
6. Pyroaurite type sorbent is expected to have double layer hydroxides, oxides and other functional intercalating carbonate ion in their inner layers (Seida et al. 2001). Functionalisation can enhance its sorptive properties for specific needs.

MATERIALS AND METHODS

Domestic wastewater samples were collected from a drain near St. John's Crossing of Agra city. The pH and EC of the samples were measured on the site and the other parameters were analysed in the lab according to the APHA (1998). Samples were stored at temperature below 4ºC to avoid any change in the physico-chemical characteristics. The COD of the samples were estimated by dichromate oxidation before and after the sorption of contaminants with sorbents.

A pyroaurite like compound (PLC) was synthesized from $MgCl_2$ and $FeCl_3$ by following the method reported (Seida et al. 2001). PLC was modified to get PTS. The modification was done with by treating PLC with cetyltrimethyl ammonium bromide and dodecan-1-thiol.

Flyash was obtained from Faridabad thermal power plant, Haryana. The flyash was derived out of the bituminous coal obtained from the Siyal and Gaddi coal mines of Bihar (India). The sample received was washed with distilled water to remove surface dust and was dried in sun. Flyash samples were stored in the laboratory in airtight plastic container. The physico-chemical characterisation of flyash was carried out using standard procedures. In addition physical properties such as density and surface area were also determined. The major components of flyash are alumina, silica, iron oxide, calcium oxide and residual carbon. However, the constituents of flyash vary according to the type of coal used and degree of combustion.

Granular activated carbon was procured from CDH, India.

The batch experiments were run in different glass flask of 250 ml capacity using shaker at average speed of 150 rpm. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant for each run throughout the experiment ensuring equal mixing. The desired pH was maintained using dilute NaOH/HCl solutions. Each flask was filled with a known volume of sample having desired pH commenced the stirring. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered through Whatmann No. 44 filter paper. The experiments were carried out under different experimental conditions.

The effect of initial COD values was investigated by keeping all the conditions constant except changing the initial COD conc. by using simulated COD bearing solutions prepared by dissolving known amount of glucose in distilled water. The residual COD concentration was determined after each run.

10 g/l of each sorbents was agitated with wastewater of COD value 600 mg/l for different time periods, 30-220 minutes. After the predetermined time intervals, the samples were withdrawn, filtered and determined the residual COD concentration.

100 ml of sample was treated with different doses of sorbents (10-70 g/100 ml) to evaluate the effect of sorbent dose. A control with 0 g/100 ml was used to estimate sorption from any other matter than sorbent. The samples were agitated for specific time, filtered and then analyzed for the residual COD.

The pH effect was studied taking a specific concentration, adsorbent dose, and contact time and varying the pH values from 2-8 using dilute NaOH/HCl solutions. The samples were agitated for specific time, filtered and then analysed for the residual COD concentration.

RESULTS AND DISCUSSION

The results observed after the physicochemical analysis of the wastewater as depicted in Table 1 indicate that the domestic wastewater is highly polluted with the organic load and suspended matter. Organic load is depicted in terms of COD and BOD .

Table 1. Physico-chemical properties of domestic wastewater

	Parameter	Value	Maximum permissible limit*
1.	pH	7.2	8-8.5
2.	Electrical conductance or EC (µmhos/cm)	1330	400
3.	Temperature (°C)	20.5	16-32
4.	Turbidity (NTU)	320	10
5.	Total solids (mg/l)	3491	…….
	Total suspended solids (mg/l)	341	…..
6.	Total dissolved solids (mg/l)	3150	2000
7.	Chemical oxygen demand (mg/l)	780	6
8.	Biochemical oxygen demand (mg/l)	383	6

- These limits are for drinking water.

The COD value is much higher than the permissible limit. The composition of flyash in Table 2 indicates that the flyash is predominantly silicious followed by the insoluble oxides of aluminium, iron, calcium, magnesium, titanium, alkali oxides and a negligible amount of phosphorus pentoxide and sulphur oxides. In case of flyash as an adsorbent the metal salts hydrolyse in the presence of natural alkalinity to form metal hydroxides. The multivalent cations present in flyash can reduce the zeta potential while the metal hydroxides are good adsorbents. They form monomolecular layer on the surface of suspended organic matter and removes it by enmeshing them and settling.

Table 2: Characteristics of sorbents

Characteristics	PTS	PLC	AC	FA
Density (g/cc)	2.20	2.50	1.40	1.80
Bulk density (g/ml)	1.6	1.8	1.20	1.21
Moisture (%)	11.31	16.31	3.61	15.0
Ash (%)	9.65	12.65	3.32	12.32
Volatile matter (%)	6.74	5.74	9.39	3.26
Loss of ignition	5.02	4.02	3.83	13.02
Chemical Analysis				
SiO_2 (%)	2.00	2.00	7.05	4.20
Al_2O_3 (%)	0.02	0.02	2.05	2.10
CaO (%)	0.12	0.12	0.04	0.21
Fe_2O_3 (%)	5.32	5.02	1.23	0.30
MgO (%)	3.02	3.00	1.10	0.10
Surface area (m^2/g)	590.0	470.0	538.2	378.5

Figure 1 represents the effect of initial COD value on % COD reduction by PTS, commercial activated carbon and flyash at the optimum pH, adsorbent dose and the contact time. It is clear from Tables 4-6 that PTS seems to be fairly active adsorbent even at higher initial concentrations. At lower initial concentrations, the ratio of the initial number of moles available to the adsorbent surface area is low and subsequently the fractional adsorption becomes independent of initial concentration. At higher concentrations, the available sites of adsorption become fewer and hence the % removal of COD depends upon the initial concentration. The COD removal of over 90% -96% obtained with PTS within the concentration range investigated. The comparison in trend of % COD reduction by flyash with respect to commercial activated carbon under this condition is depicted in Figure 1.

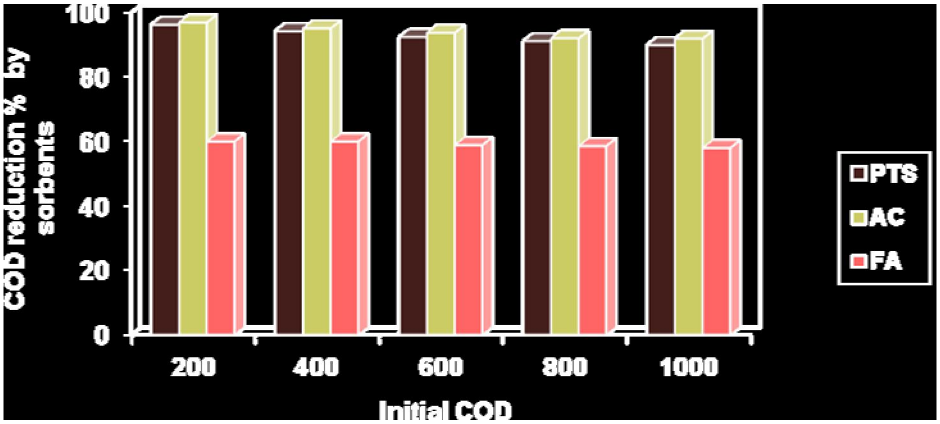

Figure 1. COD reduction % by sorbents at pH 6, sorbent dose 10 g/l, contact time 1 h, temperature 20.5°C and rpm 150

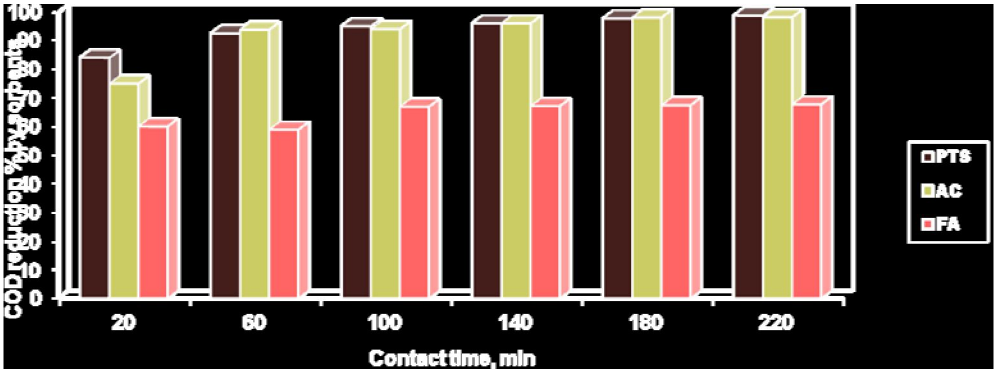

Figure 2. COD reduction % at different contact times and at pH 6, sorbent dose 10 g/l, initial COD 600 mg/l, temperature 20.5°C and rpm 150

Figure 2 represents the percent removal of COD at different contact times by PTS, flyash and commercial activated carbon. It seems that COD removal has been achieved to the extent of more than 98.7, 98.1 and 67.8 % by PTS, AC and FA respectively at a maximum time period of 220 minutes and the trend of percent COD reduction with PTS was comparable to that of commercial activated carbon.

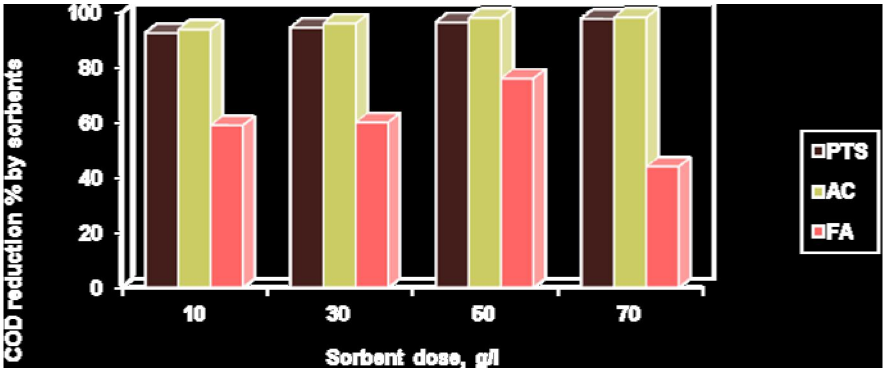

Figure 3. COD reduction % using different sorbet doses at pH 6, initial COD 600 mg/l, contact time 1 h, temperature 20.5°C and rpm 150

Figure 3 indicates the effect of adsorbent dose on the percent COD reduction by these sorbents. After that the equilibrium was set up by further addition of adsorbent dose. Flyash did not show the same trend to that of commercial activated carbon. The results showed the tremendous increase in percent COD removal with the increment of adsorbent dose, owing to the increase in the number of sites. At lower doses, the significant small adsorption is possibly due to the saturation of surface active sites with the adsorbate molecules. Table 6 depicts the effect of pH on percent COD reduction by PTS, AC and FA. The runs were taken at the constant initial COD concentration, adsorbent dose and the contact time. The results indicate that at pH level 6.0, the sorbents have consistently higher adsorption capacity f or COD.

At high pH the capacity of the adsorbent get recessed (Figure 4). The reason for the better adsorption capacity observed at low pH levels may be attributed to the larger number of H^+ ions present, which in turn neutralise the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher pH. The reduction in adsorption may be possible due to the abundance of OH^- ions, causing increased hindrance to diffusion of organics (contributing to COD) ions. Oxides of aluminium, calcium, silicon, iron etc. are abundant in flyash that adsorb contaminants.

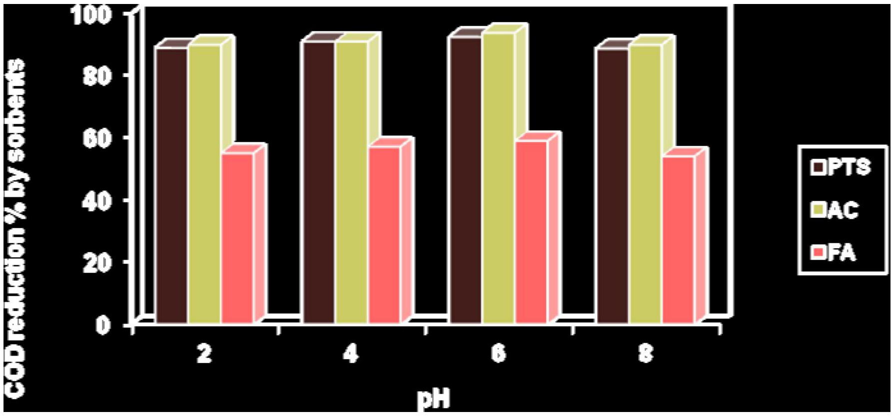

Figure 4. COD reduction % at different pH values and at contact time 1 h, sorbent dose 10 g/l, initial COD 600 mg/l, temperature 20.5°C and rpm 150

CONCLUSIONS

- The results have indicated that the COD can be reduced upto the extent of 90 % by PTS or AC while use of flyash reduce COD upto about 60 %.
- Trend of % COD removal by PTS is fairly comparable to that of commercial activated carbon.
- Though its capacity of FA is lower than that of PTS or AC, the low material cost makes it an attractive option for the treatment of domestic wastewater.
- The treatment of domestic wastewater can be done not only by PTS or AC but also by flyash generated from thermal power plant or any factory to reduce the organic load.

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REMOVAL OF HEAVY METALS FROM ELECTROPLATING EFFLUENTS BY CARBONIZED AGROWASTES

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Abstract

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 work aimed to evaluate the feasibility of using powdered pseudoactivated carbon prepared from agrowastes for the removal of heavy metals from electroplating effluents. 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 concentration 1-20 mg/l at sorbent dose 1 g/l, pH 4.8, temperature 25°C, rpm 250 for 5 h. The sorption increased with increasing contact time but the equilibrium was attained in 2 h 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**.**

INTRODUCTION

In India, there are over 50,000 large, medium and small electroplating units mostly scattered in the urban areas. Most large units are captive to some other large industrial units (Chauhan and Chauhan 2002). Medium units cater to selected business groups as feeder units. Small units mostly carry out job plating where, unlike captive and feeder units, most of operations are done manually in residential areas as family owned business and there is no space for effluent treatment. The variety of processes and methods of operation in the metal finishing industry give rise to a wide range of effluent compositions (Pigage et al. 2002). The processing baths contain high concentration of potentially polluting materials. In general, the wastewater can be expected to contain cyanides of potassium or sodium, complex cyanides, copper, nickel and zinc in acid solution, hexavalent chromium, oil wastes and solvents. Due to proprietary nature of many products used in the metal finishing, the precise composition is quite often not known. Dissolved chemicals and metals, which are not toxic to aquatic life at very low concentration levels are, however, the major concern. The permitted levels of metal contaminants in the electroplating wastewater to be discharged, as applicable in various parts of the world as well as in India, are very low but the electroplating effluents have their very high levels. A typical wastewater from an electroplating industry is likely to have in ppm 100-500 suspended solids, 20-100 Cr(VI), 30-150 total Cr, 15-90 CN^-, 5-25 Cu, 15-70 Ni and 10-200 Zn whereas the permitted levels of these contaminants in the electroplating wastewater to be discharged are 100, 0.1, 2.0, 0.2, 2.0, 2.0 and 5.0 ppm respectively. The pH is in the range of 4-10 that must be changed to 6.5 to 7.5 before water is released into the environment.

Though activated carbon is an ideal adsorbent for organic matter due to its organophilic character, it is not economical for wastewater and soil treatment owing to its high production and regeneration costs, and about 10-15% loss during regeneration by chemical or thermal treatment. High cost of activated carbon and synthetic resins has prompted search for substitutes that are abundant, cheap, renewable and ecofriendly (Dakiky et al 2002; Buerge-Weirich et al 2002). So the use of agricultural residues such as saw dust or industrial by-products like bagasse have received considerable attention (Achari and Anirudhan 1995; Gaghate et al. 1990; Siddique et al. 1999; Haribabu 1992; Rai and Surendra 1999; Rangaraj et al. 1999; Selvakumari et al. 2001; Singh et al. 2000). Most of these materials contain functional groups associated with proteins, polysaccharides like lignin, cellulose and hemi cellulose. The pollutant uptake is believed to occur through coulombic attraction and ion exchange processes involving these groups. Though these materials generally do not have high sorption capacity as compared to activated carbon, they are plentiful, inexpensive and renewable. This offers an attractive approach to the removal of metal cations in solution. The sorption capacity of these materials could be enhanced by various physicochemical modifications to improve their physical and structural properties making them more suitable for full-scale filter applications. The goal of this research is to evaluate the ability of coconut coir carbon (CCC), sagaun sawdust carbon (SSC), wheat stem carbon (WHC) and rice husk carbon (RHC) to remove heavy metals from the electroplating effluent as effective, low cost, biomass sorption media.

MATERIALS AND METHODS

Sagaun saw dust used in this study was collected from the saw machine at Panchkuian, Agra. Coconut coir, rice husk and wheat stem were obtained from the local market. All the four agrowastes were dried in the sun, crushed, washed thrice with distilled water and rinsed with 1% HCl to remove water soluble impurities particularly metal ions and surface adhered particles. Then they were kept in 0.1 N NaOH solution overnight to remove lignin and in 0.1 CH_3COOH to remove alkalinity developed due to NaOH. Thereafter, they were washed well with distilled water till the wash water became colourless. Now they were dried at 110ºC in an oven for 2 h to get rid of moisture and other volatile impurities. Their carbons were prepared by keeping 4 parts of the above agrowastes with 3 parts by weight of conc. H_2SO_4 in an air oven maintained at 150°C for 24 h. The carbonized agrowastes were washed with distilled water to remove free acid (SO_4^{2-} ions). Then they were soaked in 1% w/v sodium carbonate solution overnight to remove any residual acid. Again they were washed with distilled water and dried at 110°C for 2 h. The carbons so obtained were ground in a mortar with a pestle and sieved through a standard sieve to get the particle size less than 300 microns throughout the study.

All chemicals used were of analytical grade unless otherwise specified. Distilled deionized water (DDW) was used throughout the experiment. Five standard solutions of 1, 5, 10, 15 and 20 mg/l concentrations of Cr, Ni, Cu and Zn for instrument calibration and sorption study were prepared by diluting their stock solution of 1 g/l, i.e., 1 ml □1 mg metal. To prepare the Cr(VI) stock, 2.828 g anhydrous $K_2Cr_2O_7$ was dissolved in about 200 ml DDW, 1.5 ml conc. HNO_3 and diluted to 1 litre with DDW. The stock solution of Ni, Cu and Zn were prepared by dissolving 1.000 g of 99.5% AR 325 mesh metal powder from CDH, New Delhi in a minimum volume of 1:1 acid (HNO_3 for Ni and Cu, and HCl for Zn) and diluting to 1 litre with 1% (v/v) acid.

The capacity studies were carried out by transient batch tests. In 25 numbers (5 concentrations of 4 metals each + 5 controls one for each) of 100-ml capacity PVC bottles with screw caps, 0.05 g of sorbent was added to each bottle of 5 sets, each set having 6 bottles 5 for different concentrations of a metal and 1 for its control. 50 ml of the metal solution or effluent was added to each bottle. The solution was buffered with 0.07M sodium acetate - 0.03 M acetic acid to pH 4.8. Each bottle was shaken in a reciprocating shaker at 180 rpm for 5 h at room temperature, and the metal concentration was measured per hour until the solution reached equilibrium. The controls without sorbent are to demonstrate metal uptake due to the sorbent, not from other sources such as the walls of the container, centrifuge tube etc. The contents were centrifuged at 2000 rpm for 10 min and the supernatant liquid was filtered using a 0.45-µm membrane filter. The filtrate was analysed for metal ions. The initial and final concentrations of the metal solutions were determined using a Perkin-Elmer AAnalyst 100 AAS by Standard Methods (APHA et al. 1998). Experiments were triplicated and results averaged.

RESULTS AND DISCUSSION

The characteristics are listed in Table 1. Such carbons are expected to be more than four times more effective than raw agrowastes (Manju and Anirudhan 1997; Perisamy and Namasivayam 1995).

Table 1. Characteristics of Adsorbents

Parameters	RHC	CCC	WSC	SSC
Composition (in %)				
Moisture	3.82	4.96	5.67	4.22
Ash	4.56	7.85	5.68	8.36
Carbon	79.89	80.32	78.9	81.73
Silica	2.76	4.36	3.02	4.64
Sodium	0.13	0.11	0.17	0.09
Potassium	0.29	0.31	0.27	0.23
Calcium	0.35	0.39	0.41	0.32
Magnesium	0.03	0.02	0.07	0.01
Phosphorous	0.05	0.04	0.06	0.03
Iron	0.27	0.19	0.32	0.12
Miscellaneous	7.85	1.45	5.34	0.25
Properties				
pH	8.32	7.64	7.34	7.83
Conductivity (µS/m)	0.92	0.80	0.75	0.62
Specific gravity (g/L)	1.20	1.34	1.10	1.12
Porosity (ml/g)	1.01	0.92	0.83	0.72
Surface area (m^2/g)	456	397	328	298
Cation exchange capacity(meq/g)	0.70	0.90	0.53	Nil

The physicochemical properties of carbonized agrowastes vary widely from plant to plant and method to method of carbonization. They depend on variety of a plant and area in which it is cultivated, temperature of carbonization, operational features and efficiency of the heating equipment like oven or furnace, The peaks of their X-ray diffractogram can be used to identify major components as crystalline quartz, amorphous silica, calcium orthosilicate, cristobalite, sillimanite, crystalline carbonate etc. (Swamy et al. 1998). Their scanning electron micrographs can depict their morphology particularly linear or curved type fibers with holes in fibers and at other places in skeletal structure. The number and size of pores of a carbon can also be determined. The greater the number and larger the size of pores but the smaller particle size make a better sorbent. The bands of their FTIR spectra can indicate the presence of carboxy, hydroxy, sulphonic etc. groups responsible for cation exchange.

Table 2. Effect of Cr, Ni, Cu and Zn concentration on their % removal at agitation time 4 h, rpm 240 and sorbent dose 1 g/l, pH 4.8 and temperature 25°C

Metal	Concentration (mg/l)*	RHC	CCC	WSC	SSC
Cr(VI)	1	92.1	90.9	88.3	85.1
	5	89.5	88.2	84.5	80.0
	10	84.2	82.4	76.8	70.9
	15	75.7	71.1	65.9	58.4
	20	68.1	62.3	56.1	48.5
Ni(II)	1	97.6	95.9	94.3	92.8
	5	97.0	94.7	92.7	90.4
	10	95.5	91.9	88.4	84.5
	15	91.3	86.0	79.6	71.2
	20	84.2	76.6	70.9	62.9
Cu(II)	1	94.2	93.6	91.9	88.0
	5	92.7	91.7	89.0	83.6
	10	89.2	86.9	83.9	76.1
	15	81.2	78.9	73.4	62.3
	20	72.5	68.6	63.4	54.1
Zn(II)	1	95.4	94.7	92.3	90.8
	5	94.2	93.2	90.6	87.0
	10	91.5	89.4	84.5	80.2
	15	85.2	80.9	75.2	68.1
	20	78.5	72.1	64.2	56.5
Cr(VI)	18.0	67.4	61.0	55.7	47.2
Ni(II)	18.9	83.0	75.2	68.5	60.3
Cu(II)	8.6	89.0	86.5	83.4	75.5
Zn(II)	15.6	81.0	75.4	68.3	60.7

*The second set of data is for metal ions present in electroplating effluents.

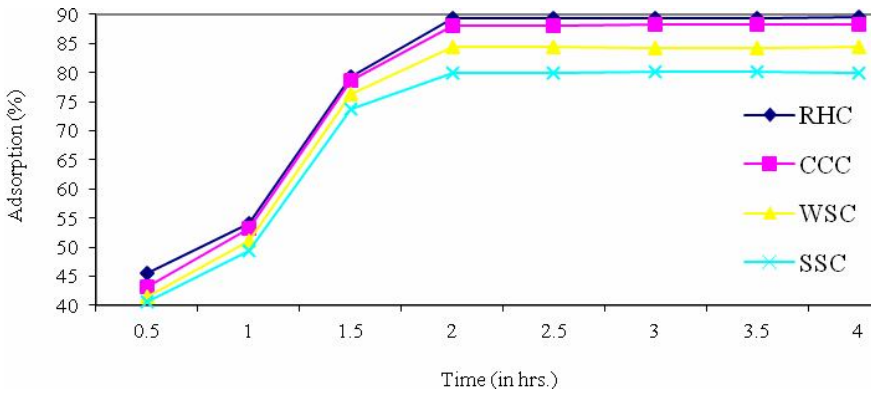

Figure 1. Effect of contact time on the % removal of Cr at 5 mg/l concentration, sorbent dose 1 g/l, pH 4.8 and temperature 25°C

The effect of contact time on sorption was also investigated (Figure 1)

The uptake of metal ions at 1, 5, 10, 15 and 20 mg/l concentrations by different sorbents was thus calculated and results are listed in Table 2.

The data were analysed using the Freundlich and the Langmuir equations:

$$\ln a = \ln k + 1/n \ln c \qquad \text{Freundlich equation}$$

$$c/a = 1/Qb + c/Q \qquad \text{Langmuir equation}$$

where a (mg/g) is the metal sorbed per unit mass of sorbent (a = x/m where x mg of metal is sorbed on m grams of sorbent), c (mg/l) is equilibrium concentration in aqueous phase, k (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively, Q (mg/g) and b (l/g) are Langmuir constants related to adsorption capacity of sorbent and adsorption maximum (energy of adsorption) respectively. The Langmuir constants were calculated at five initial concentrations under optimal conditions (Table 3).

Table 3. Comparison of Langmuir and Freundlich constants and correlation coefficients (R^2 values) for the sorption of heavy metals by RHC, CCC, WSC and SSC

System	Langmuir constants and R^2			Freundlich constants and R^2		
	Q, mg/g	b, 1/g	R^2	k, mg/g	1/n	R^2
Cr/RHC	15.5637	0.7730	0.9975	7.422	0.5057	0.9665
Cr/CCC	14.3753	0.7581	0.9986	6.985	0.4686	0.9529
Cr/WSC	13.1134	0.6130	0.9998	6.199	0.4605	0.9759
Cr/SSC	11.4383	0.5978	0.9999	5.102	0.4311	0.9531
Ni/RHC	18.7713	2.3191	0.9993	16.956	0.4823	0.9501
Ni/CCC	17.1763	1.4426	0.9998	11.884	0.4753	0.9484
Ni/WSC	15.8784	1.1181	0.9984	9.430	0.4782	0.9503
Ni/SSC	14.0016	0.9786	0.9965	7.413	0.4551	0.5266
Cu/RHC	17.1083	1.0063	0.9991	9.697	0.4839	0.9512
Cu/CCC	15.6278	0.9955	0.9998	8.936	0.4718	0.9523
Cu/WSC	14.2539	0.8527	0.9995	7.511	0.4501	0.9530
Cu/SSC	12.2523	0.6460	0.9977	5.539	0.4505	0.9534
Zn/RHC	18.3009	1.1852	0.9979	11.151	0.5088	0.9584
Zn/CCC	16.3204	1.1634	0.9987	9.922	0.4744	0.9488

Zn/WSC	14.9322	0.8557	0.9998	8.269	0.8023	0.9445
Zn/SSC	12.5572	0.8492	0.9139	6.878	0.4147	0.9468

Sorption capacity is found to decrease with increase in metal concentration. The higher uptake at lower initial concentration can be attributed to the availability of more isolated metal ions. Sorption rate is very rapid during initial period of contact due to the availability of more sites for sorption and more than 60 per cent of sorption is reached within 1 hour. However, equilibrium was attained after 2 h for Cr, 3 h for Zn, 3.5 h for Cu and 4.0 h for Ni. RHC could remove greater amount of these metals than any other carbon studied. It was found to remove 92.1% Cr (VI), 97.6% Ni, 94.2% Cu and 95.4% Zn at concentration 1 mg/l, sorbent dose 1 g/l, rpm 240, agitation time 4 h, pH 4.8 and temperature 25°C. The order of metal removal capacities for these chemical adsorbents was RHC > CCC > WSC > SSC. The order of removal/sorption of metals was Ni > Zn > Cu > Cr. The effect of various parameters affecting the adsorption such as initial metal concentration, adsorbent dose, contact time and pH was determined. Adsorption decreases with rise in metal concentration but increases with increase in adsorbent dose.

The rate of adsorption is high in the beginning as sites are available and unimolecular layer increases. Adsorption and desorption occur together and rates become equal at a stage called adsorption equilibrium when isotherms are applied. That is why there is little increase in % removal on increasing contact time from 4 to 5 h. The subsequent slow rise in curve may be due to adsorption and intra-particle diffusion taking place simultaneously with dominance of adsorption.

The pseudoactivated carbons may consists of oxides of silicon, calcium, magnesium, iron, etc. They may have anion adsorption sites similar to minerals like alumina and clay. Such sites are aquo groups (—M—OH$_2^{-}$) and hydroxo groups (—M—OH). The surface chemistry of an oxide in contact with an aqueous solution is determined to a large extent by deprotonation or a hydroxyl ion association reaction. However, some evidences suggest that an anion like $Cr_2O_7^{-}$ can be adsorbed by ion exchange mechanism even though the surface is neutral. Had Cr(VI) not been in dichromate form, it would have been sorbed to the maximum extent based on its ionic size and potential.

The optimum pH for metal removal was found in the acidic medium (Singh et al. 2001). The reason may be attributed to the large number of H$^+$ ions in acidic medium neutralize negatively charged adsorbent surface, thereby reducing hindrance to diffusion of dichromate ions. At higher pH the abundance of OH$^-$ ions create increased obstacle to diffusion of dichromate ions.

CONCLUSIONS

The following conclusions can be drawn from the above results:

1. CCC, SSC, WSC and RHC to remove heavy metals from the effluent in the order of Ni > Zn > Cu > Cr over a wide range of initial concentration 1-20 mg/l at sorbent dose 1 g/l, pH 4.8, temperature 25°C, rpm 250 for 5 h.
2. The sorption increased with decreasing metal concentration and increasing contact time, but the equilibrium was attained in 2 h for Cr, 3.0 h for Cu, 3.5 h Zn and 4 h for Ni.
3. The order of metal removal capacities for these chemical sorbents was: RHC > CCC > WHC > SSC.
3. Electroplating effluent showed 4 to 10% lower removal as compared to synthetic standard solution under similar conditions.
4. The sorption followed Freundlich as well as Langmuir isotherms.

5. The present paper shows the possibility of using agrowastes particularly rice husk abundantly available in our country to produce cheaper activated carbons. The data thus generated may be used for designing treatment plants for industrial effluents having low levels of heavy metals and hold a promise for commercial exploitation.

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