

Preparation of Porous Carbon from Various Agricultural
Wastes and its Application for Metal Ions Recovery

September 2009

Department of Chemistry and Applied Chemistry
Graduate School of Science and Engineering
Saga University

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APPROVAL PAGE

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by
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A Dissertation submitted in partial fulfillment of the requirements for the
degree of philosophy
Doctor of Philosophy

Department of Energy and Materials Science
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ABSTRACT

PREPARATION OF POROUS CARBON FROM VARIOUS AGRICULTURAL WASTES AND ITS APPLICATION FOR METAL IONS RECOVERY

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Carbons were prepared from biomass like rice husk, barley and wheat straws by single-step carbonization at different carbonization temperature from 600-1000 °C. The evolution of pore structure and surface chemistry during carbonization was investigated through surface area measurement. Potential of zero charge (PZC) measurement reveals that the surface of carbons was positively charged at acidic pH. Thus these biomass carbons were expected to adsorb metal ions which exist as anionic form in aqueous solution at acidic pH. The ability of using low-cost agro-waste carbon for Cr(VI) removal from the aquatic environment was studied in terms of solution pH, equilibrium Cr concentration and contact time. The optimum pH value was 2 for Cr(VI) adsorption and Cr(VI) removal was interpreted by an adsorption-coupled reduction mechanism which was supported by kinetic data. The effects of hydrochloric acid concentration, metal ion concentration, and contact time on adsorption of some precious metals and base metals were examined in batch mode. The carbon exhibited selectivity only for precious metal ions tested, but was inert to base metal ions such as Cu(II), Fe(III), and Ni(II). Column test for metal solution containing Au(III), Pt(IV), Pd (II), and Cu(II) in mutual system was performed on wheat straw carbon to determine the applicability of this carbons on adsorptive separation of precious metals in continuous operation. Oxidation of carbonized biomass was performed using HNO₃ to introduce acidic functional groups on the carbon and to make it cation exchanging adsorbent. The effects of oxidation using HNO₃ on the properties of the carbonized wheat and barley straw were investigated by measuring different properties such as specific surface area, PZC, total surface acidic groups as well as FTIR and TG-DTA analysis. The oxidized carbon samples were compared with the unoxidized original carbon samples for Cr(III) adsorption. It was observed that the oxidized carbons exhibit high adsorption efficiencies for Cr(III) ions compared to the original carbonized straws and this can be correlated to the decrease in PZC which is mainly due to the increase in carboxylic functional groups in the oxidized carbonized straws and these are responsible for their cation exchange phenomenon.

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Introduction

1.1. Activated carbon

Activated carbon is a porous material, a char which has been subjected to reaction with gases, sometimes with the addition of chemicals (*e.g.* ZnCl_2) before, during or after carbonization in order to increase its adsorptive properties.

1.1.1. Carbon materials

In the periodic table, the element carbon occupies quite a unique position, atomic number of six with four outer electrons capable of multi-bonding (sp -linear, sp^2 -in ring, and sp^3 , as in diamond). It is of low atomic weight (12.011 amu). It is an element of prehistoric discovery and is ubiquitous being found in meteorites and in abundance in suns, stars, comets and the atmospheres of most of the planets. That is, it is an element, an atom, of significant stability. The atmosphere of the planet Mars contains 96.2vol% of carbon dioxide. It is an element of immense versatility, combining with hydrogen, oxygen, nitrogen and other elements to form at least 10 million compounds. All forms of life are existed from carbon and activated carbon is manufactured from carbon containing organic materials like woods, nutshells, and coals of various ranks [1].

Family of carbons like diamond, activated carbon, lamp black *etc* is all made from carbon materials from a structural point of view. But they possess different specific properties and have a unique identity due to intimate functions of structure within each carbon. The structures in all known carbon (apart from diamond) forms are considered as a continuous decrease in the degree of order from the single-crystal hexagonal graphite to the most disordered (there is never total disorder) of the porous

carbons and the glassy carbons with their closed (inaccessible) porosity. Within hexagonal graphite, the layers of hexagonal arrangements of carbon atoms are described as graphene layers. These layers do not lie immediately above and below each other but are displaced to form an ABABAB sequence as shown in Fig. 1.1. The density of hexagonal graphite is $\sim 2.25 \text{ g/cm}^3$ (3.52 g/cm^3 in diamond). The distance between the layers is 0.335 nm and the distance between two bonded carbon atoms is 0.142 nm . Within the graphitic layers, the bonding is trigonal sp^2 -hybrid σ -bonds with delocalized π -bonds within the layers. The interlayer spacing of 0.335 nm , being larger than the 0.142 nm of the C – C bond, indicates no chemical bonding between the layers, the forces of attraction being limited to van der Waals forces. This distance is between the values of 0.153 nm and 0.132 nm for $Csp^3 - Csp^3$ bonding as in ethane, and $Csp^2 = Csp^2$ bonding as in ethene. Resonance considerations indicate that the C to C bonding within a graphite layer has about one-third double-bond character. Such a graphite structure is referred to as AB graphite [2].

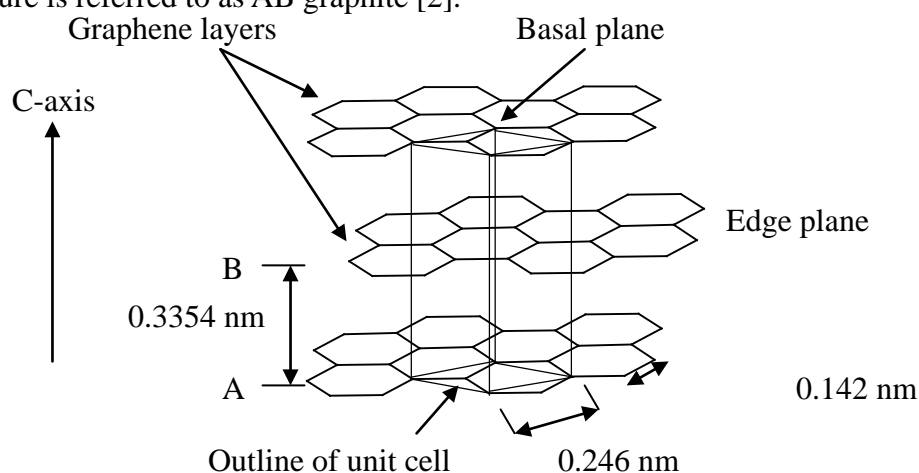


Fig. 1.1. The structure of hexagonal graphite, with trigonal planar bonding within the graphene layers.

Activated carbon is a member of a family of carbons and it is porosity (space) enclosed by carbon atoms which imparts their dominant characteristics of adsorption. Activated carbon is a unique material because of the way it is filled with “holes” (voids, spaces, sites, pores, whatever) the size of molecules. The special thing about these holes is, although they are spaces of zero electron density, these pores possess intense van der Waals force from the near proximity of carbon atoms and these are responsible

for the adsorption process [3].

There are several hundred commercial activated carbons available, with different sizes of porosity with specific applications. The common structure in activated carbons is the assemblies of defective graphene layers.

1.1.2. Parent Materials for Carbons

Entire world's flora is capable of providing a porous carbon on carbonization in an inert atmosphere. However, the casual production of activated carbon, capable of performing with efficiency the required industrial applications, does not happen. The commercial activated carbons on the market today are the result of continuous and intensive research and development toward optimization of application. The economics and availability of parent materials are as important (may be more so) as extents of available internal pore volumes (surface areas) associated with the right kind of porosity and surface chemistry [4].

The availability of activated carbon for industrial use has much to do with accessing resources, renewing resources and processing to rigid specifications to control specific industrial applications. Only a handful of resources are used for activated carbon production, including coals of several ranks and peat. For this reason, the assortment of active carbons is limited and they are expensive [5]. This has increased continually the amount of carbon dioxide and other hazardous components in the earth atmosphere. As an option for preventing this disaster, uses of plant origin (biomass) materials regarded as carbon dioxide neutral have been considered as an alternative parent materials for carbons. Of the other resources which frequently come up for consideration are nut shells, coconut shell, rice husk, woodcuttings, casings from coffee beans and many other organic waste materials [6-9]. The use of plant raw materials as a feedstock makes it possible to obtain almost ashless active carbons because the concentrations of mineral components in these materials are low. There is global interest in the conversion of agrowaste into carbon adsorbents but collection from separated areas, transportation, bulk availability and seasonal variations in quality

and availability are some of the demerits of using agrowaste as parent materials [1].

All carbonaceous materials can be converted into activated carbon, although the properties of the final product will be different, depending on the nature of the raw material used, the nature of the activating agent, and the condition and activation processes [10,11]. Activated carbon is a member of a family of carbons ranging from carbon blacks to nuclear graphites, from carbon fibres and composites to electrode graphites, and many more. All come from organic parent sources but with different carbonization and manufacturing processes. The wide range of carbon artifacts available has a common ancestry that is single-crystal graphite. All carbon forms (except the mineral diamond) are related to the graphite lattice in some way with each form of carbon representing one of an infinite number of assembled defective graphene layers, some very defective indeed.

1.1.3. Preparation of carbon

Carbon materials result from the carbonization of organic materials; that is, their heat treatment in an inert atmosphere to a required temperature resulting in increases in carbon contents and decrease in contents of heteroatoms [12]. Such carbonizations occur in the solid, the liquid and the gas phases.

Solid – phase carbonization means heating the parent materials, almost always being a macromolecular system, which is accompanied by the evolution of gases and liquids of low molecular weight resulting from the decomposition processes as shown in Fig.1.2. Consequently, the resultant carbon is a “pseudomorph” of the parent material, having more or less the same original shape but it is now of a lower bulk density. A solid – phase carbonization process is a progressive decomposition which will cease when the heat treatment is stopped. Increasing the heating temperature results in the formation of progressively more stable intermediate structures. The carbonization process essentially is the conversion, by progressive heating, of a three-dimensional organic macromolecular system to a three-dimensional macro-atomic network of carbon atoms. As small molecules, such as water, methanol

and carbon dioxide are eliminated from the organic system, so the resultant free radicals are removed by movement of atoms over short atomic distances (< 1 nm) to create an intermediate stable phase of higher carbon content. The process does not produce a continuous solid phase but produce a network of porosity. As the carbonization temperature continues to rise so the extent of this space network increases as well as its dimensions, length and breadth, to a maximum. With further increase in heating temperature above about 800°C , accessibility to adsorbate gases decreases as cross-linking of carbon atoms reduces space between atoms and essentially closes off porosity to an adsorptive gas. Carbonizations in the solid phase cannot permit any internal recrystallization, resultant structure being quite disordered but never disorganized and constitute what are termed non-graphitizable carbons and are isotropic with considerable microporosity [1].

Structure produced by carbonization may be considered as segments of graphene sheets (not a three – dimensional segment) of different sizes reaching nanometer dimensions and degree of perfection (holes, non – planarity, linear carbon atoms and the presence of heteroatoms), bonded together in an infinite number of ways. The random bonding together of these small defective polycyclic groups of carbon atoms, with linear carbon atoms, creates space (imperfect packing) called porosity. The method of preparation forms the basis of much carbon chemistry. The different arrangements of segments or groups of carbon atoms confer on carbons their extremely wide range of properties (*i.e.* physical, chemical and mechanical) as a result of which carbon materials have an extensive range of industrial applications [1].

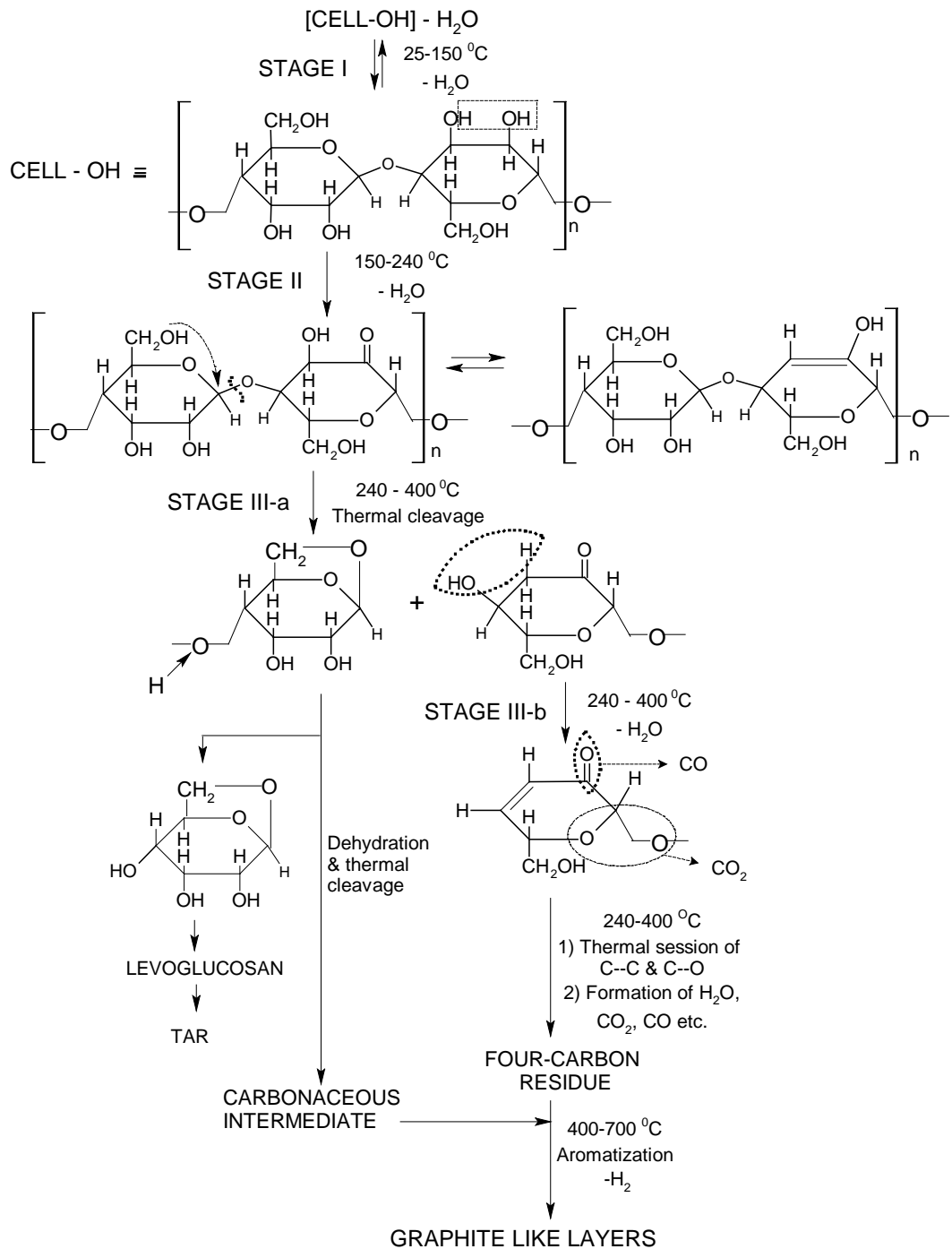


Fig.1.2. Proposed mechanism for the conversion of cellulose to carbon.

Liquid-phase carbonization occur *via* liquid-phase leading to formation of graphitizable, anisotropic aromatic, nematic crystals (called mesophase) formed as a result of growth and self-assembly of the constituent polycyclic aromatic molecules of the parent material. In gas-phase carbonization the gaseous mixture like methane, propane or benzene are carbonized (cracked or pyrolysed) at a low relative pressure

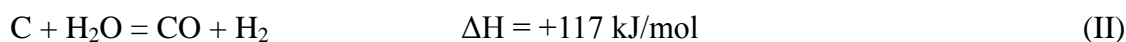
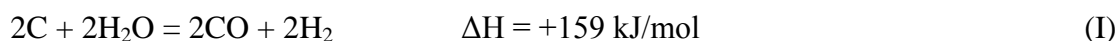
usually brought about by dilution with helium. The fragments of the pyrolyses (radicals) from the parent feedstock interact with a suitable substrate and, by a mechanism involving carbon atom movement, the hexagonal lamellar structure of graphite is established. Gas-phase carbonizations produce highly graphitizable materials, produced by growth involving deposition of carbon atoms from the gas phase (methane or benzene). These pyrolytic (deposited) carbons have a role in controlling the diameters of entrances to porosities of some activated carbons, and for the carbon-lithium battery [1].

1.1.4. Activation process

Activated carbon (AC) does not just happen; it has to be synthesized. The porosities of a carbon, as initially prepared by carbonization, are not sufficiently developed for most applications and some amelioration is a prerequisite step. This is done in several ways involving creation of further porosity, widening of existing porosity, modifications to the surfaces of porosities and also modifying the carbonization process itself. There are two industrial processes used to maximize the adsorption potential of carbonaceous material.

1.1.4.1. Physical activation

Thermal or physical activation is a process of selective gasification (removal) of individual carbon atoms. Physical activation is made using either carbon dioxide or steam or mixtures of these two gases [13]. Carbon atoms can be removed from within porous carbons by gasification using carbon dioxide or water vapor, usually at 800-900°C according to following stoichiometric equations, equation I and II [1]. Activation by carbon dioxide and steam produce carbons with different porosities.



1.1.4.2. Chemical activation

Chemical activation is a process of co-carbonization by additions of such material as phosphoric acid (H_3PO_4), or zinc chloride ($ZnCl_2$) or potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) [14,15]. Mechanism for these activations is all different, with zinc chloride promoting the extraction of water molecules from the lignocellulosic structures of parent materials, and phosphoric acid combining chemically within the lignocellulosic structures. There is no selective removal of carbon atoms as during physical activation and carbonization yields are improved.

As some industrial adsorption processes require “fine-tuning” of the porosity of a carbon, it is possible to combine thermal and chemical activation processes to obtain a desired activated carbon.

1.1.5. Application of activated carbon

Activated carbon is a unique material with its immense capacity for adsorption from gas and liquid phases. It occupies a special place in terms of producing a clean environment involving water purification as well as separations and purification in the chemical and associated industries. In these roles, it exhibits a remarkable efficiency as the international production is a little more than a million tones per year, with perhaps 2 million tones being in continuous use. Broadly AC has been used for three main purposes [1].

1. AC is dominantly used for purposes of adsorption in liquid-phase. The wide-ranging scenarios for AC are:
 - Drinking water availability, to improve taste, smell and color including removal of chlorinated compounds and other volatile organic carbons (VOCs).
 - Improvement to ground water purity, contaminants coming from disused sites of heavy industries.
 - Treatment of both industrial and municipal wastewater.
 - Mining operations require feed water treatment, metallic ion adsorption (gold

and other metals), adsorption of excess flotation reagents and adsorption of natural organic matter (NOM).

- Pharmaceutical processes, including purification of process water, use with fermentation broths and purification of many products.
 - The food, beverage and oil industries for removal of small, color and unacceptable tastes.
 - The dry-cleaning industries require purification of solvents.
 - The electroplating industries require purification of wastewaters containing Pb, Cr, *etc.*
 - Household water purification, cleaning of aquaria and use in oven-extract hoods.
 - The sugar and sweetener industries need decolorization agents for the production of white sugar, *etc.*
2. AC in different forms (granular, extruded, fiber or cloth) is used for production of pure gases in the chemical industry, to reduce pollutant gases to very low concentrations in a single stage, in protection against poisonous gases, in air conditioning, for removal of oil from compressed air, to separate gases in mixtures by sieving, *etc.*
 3. Carbon materials have been used for some time in heterogeneous catalysis, acting as direct catalysts or as a catalyst support. Catalytic particles can be supported within the porosity to promote required catalytic conversions.

1.1.6. Adsorption mechanism

Microporous carbons have a unique structure which essentially is a three-dimensional net-work, or labyrinth of carbon atoms some in hexagonal arrangements and some as individual carbon atoms bonded together extremely close but not close packed. This bonding arrangement results in space existing between the atoms to create an interconnecting three-dimensional passageway in which every space unit has a connection to all others within the carbon. The dimensions of the passageway (width) are those of molecules, about 0.5 nm, such that any molecule which enters into this space is subjected to intense dispersion forces from the carbon atoms (about eight

per space) which make up the “surface” of the space. These forces can “trap” the molecule for periods of time much longer than on an open surface and so the phenomenon of physical adsorption of gases is generated [1].

The site, place or space where a molecule can be trapped (adsorbed) is called an adsorption site. These adsorption sites can be modified in terms of their size (widened or narrowed) and in terms of their chemical composition. The surface can be bonded to hydrogen, oxygen, chlorine, nitrogen, *etc.* to alter the polarity of the surface. Changing this polarity can enhance the adsorption process for polar molecules. The porosity can be widened by gasification with water vapor, oxygen or carbon dioxide. The parent materials may also be impregnated with zinc chloride, potassium hydroxide or phosphoric acid, these treatments improving adsorption characteristics, a process known as activation. The variables, within an adsorption system (dominantly an aqueous solution) controlling extents of adsorption include:

1. Volume of narrow micropores, < 0.7 nm (VNM – cm^3/g), including the pore-size distributions.
2. Volume of wider micropores, 0.7-2.0 nm (VWM – cm^3/g), including the pore-size distributions.
3. Volume in mesopores, >2.0 and <50 nm (VME – cm^3/g), including the pore-size distributions.
4. The parameter “surface area” is a crude parameter and fails to quantify, adequately, the capacity of the all-important micropores and their size distributions.
5. The amphoteric nature of the carbon surface as measured by pH_{PZC} and pH_{IEP} .
6. The controlled additions of surface oxygen complexes from known sources, e.g. nitric acid, H_2O_2 , *etc.*, with controlled removal of the complexes, thermally or by reaction with hydrogen at temperature $> 750^\circ\text{C}$.
7. The effects of additions of surface oxygen complexes upon pore volumes and pore size distributions (pore dimensions can be reduced).
8. The characterization of surface oxygen complexes.
9. The pH of the solution.
10. Ionic strength.
11. Temperature.

1. 2. Heavy metals and their impact on the environment

The toxicity and health hazards associated with heavy metals have been established beyond any doubts. With increasing amounts of metals unearthed, amounts of toxic heavy metals entering the environment increases. As shown in Figure 1.3., the metals ‘mobilized’ by and partially lost through growing and ever-intensifying human technological activities enter the ecosystem and start to inflict the damages as they move through from one ecological tropic layer into another. They accumulate in living tissues throughout the food chain which has humans at its top. The danger multiplies and humans eventually tend to receive the problems associated with the toxicity of heavy metals pre-concentrated from many different directions. Controlling heavy metal discharges and removing toxic heavy metals from aqueous solutions has become a challenge for the 21st century [16].

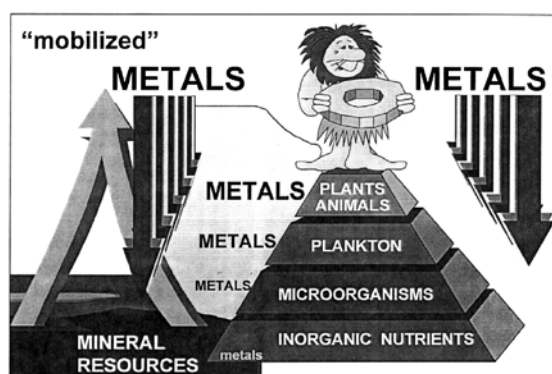


Fig. 1.3. Heavy metals pre-concentrating through food chain.

The term “heavy metal” refers to the metallic elements having density greater than or equal to 6.0 g/cm^3 . The most familiar metals are cadmium (8.65 g/cm^3), chromium (7.14 g/cm^3), cobalt (8.90 g/cm^3), copper (8.95 g/cm^3), lead (11.34 g/cm^3), mercury (13.53 g/cm^3), nickel (8.91 g/cm^3) and zinc (7.14 g/cm^3). Among these toxic metals chromium has major impact on environment and it has both beneficial and detrimental properties [17].

Unlike most organic pollutants, heavy metals occur naturally in rock-forming and ore minerals and so a range of normal background concentrations is associated with

each of these elements in soils, sediments, waters and living organisms. On an annual basis, significant quantities of various heavy metals are produced from the mining of their respective ores. In the year 2004, approximately 1.45×10^7 tons of copper was produced [18].

Industrial uses of metals and other domestic processes (*e.g.* burning of fossil fuels, incineration of wastes, automobile exhausts, smelting processes and the use of sewage sludge as landfill material and fertilizer) have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Discharged toxic metals typically include Cd, Cu, Ni, Cr, Co, Zn and Pb [19]. Table 1 outlines the industrial sources and potential for pollution for a range of metals discharged.

Table 1.1. Significant anthropogenic sources of metals in the environment.

Industry	Metals	Pollution arising	Refs.
<i>Metalliferous mining</i>	Cd, Cu, Ni(II) Cr, Co, Zn	Acid mine drainage, tailings, slag heaps	19, 20
<i>Agricultural materials</i>			
Fertilizers	Cd, Cr, Mo, Pb, U, V, Zn	Run-off, surface and groundwater contamination, plant bioaccumulation	21, 22
Manures sewage sludge	Zn, Cu, Ni, Pb, Cd, Cr, As, Hg	Landspreading threat to ground and surface water	22-24
<i>Metallurgical Industries</i>			
Specialist alloys and steels	Pb, Mo, Ni, Cu, Cd, As, Te, U, Zn	Manufacture, disposal and recycling of metals. Tailings and slag heaps	25-27
<i>Waste disposal</i>			
Landfill leachate	Zn, Cu, Cd, Pb, Ni, Cr, Hg	Landfill leachate, contamination of ground and surface water	28, 29

Industry	Metals	Pollution Arising	Refs.
<i>Electronics</i>	Pb, Cd, Hg, Pt, Au, Cr, As, Ni, Mn	Aqueous and solid metallic waste from manufacturing and recycling processes	30
<i>Metal finishing industry</i>			
Electroplating	Cr, Ni, Zn, Cu	Liquid effluents from plating processes.	31-33
<i>Miscellaneous sources</i>			
Paints and pigments	Pb, Cr, As, Ti, Ba, Zn	Aqueous waste from manufacture, old paint deterioration and soil pollution.	34
Batteries	Pb, Sb, Zn, Cd, Ni, Hg	Waste battery fluid, contamination of soil and groundwater.	35-37

While many of the heavy metals are needed by plants at the micronutrient level, higher concentrations are known to produce a range of toxic effects. The metals specially known for their high toxicity and impact are lead, mercury, cadmium, arsenic and chromium.

1.2.1. Chromium

Chromium is a member of the transition metals, in group 6, the symbol Cr and atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish, has a high melting point (1903±10° C) and is extremely resistant to ordinary corrosive agents. It is also odourless, tasteless, and malleable.

1.2.1.1. Introduction

Chromium is a naturally occurring element found in rocks, animals, plants, and soil. The name of the element is derived from the Greek word "chrōma" meaning color, because many of its compounds are intensely colored. It was discovered by Louis

Nicolas Vauquelin in the mineral crocoite (lead chromate) in 1797. Crocoite was used as a pigment, and after the discovery that the mineral chromite also contains chromium this latter mineral was used to produce pigments as well.

Chromium(0) being a member of the transition metals, in group 6, has an electronic configuration of $4s^13d^5$ due to the lower energy of the high spin configuration. Chromium exhibits a wide range of possible oxidation states. The highest oxidation state corresponds to the total of 3d and 4s electrons. The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable whereas +1, +4 and +5 are rare. Depending on the form it takes, it can be a liquid, solid, or gas. No taste or odor is associated with chromium compounds. Chromium compounds of oxidation state +6 are powerful oxidants. All (except the chromium hexafluoride) stable chromium compounds of the oxidation state +6 contain oxygen as ligand, for example the chromate (CrO_4^{2-}) and Chromyl chloride (CrO_2Cl_2) [38, 39].

1.2.1.2. Application

Chromium was regarded with great interest due to its wide range of uses in metals, chemicals, and refractories. A major development was the discovery that steel was made highly resistant to corrosion and discoloration by adding chromium and nickel to form stainless steel. Chromium use in iron, steel, and nonferrous alloys enhances hardenability and resistance to corrosion and oxidation. The use of chromium to produce stainless steel and nonferrous alloys are two of its more important applications [40].

The relative high hardness and corrosion resistance of unalloyed chromium makes it a good surface coating. A thin layer of chromium is deposited on pretreated metallic surfaces by electroplating techniques. There are two methods used to do this coating. Thin, below 1 μm thickness, layers are deposited by chrome plating are used for decorative surfaces. If wear-resistant surfaces are needed thicker chromium of up to mm thickness are deposited. Both methods normally use acidic chromate or dichromate solutions [41].

Chromium compounds have been used in dye and pigments like chrome yellow ($PbCrO_4$), chrome red ($PbCrO_4.Pb(OH)_2$), chrome oxide green (Chromium (III) oxide).

Its compound has been used in producing synthetic rubies, enamel painting, glass staining, metal polishing *etc.* [42, 43]. Chromium(III) sulfate ($\text{Cr}_2(\text{SO}_4)_3$) is used as a green pigment in paints, in ceramic, varnishes and inks as well as in chrome plating [44].

The toxicity of chromium(VI) salts is used in the preservation of wood, for example chromated copper arsenate is used in timber treatment to prevent wood from decay fungi, wood attacking insects, including termites, and marine borers [45].

Chromium salts, especially chrome alum and chromium(III) sulfate, are used in the tanning of leather [46]. The chromium(III) stabilizes the leather by cross linking the collagen fibers within the leather. Chromite as refractory materials is used to make molds for the firing of bricks [47]. Trivalent chromium (Cr(III) or Cr^{3+}) is required in trace amounts for sugar and lipid metabolism in humans and its deficiency may cause a disease called chromium deficiency. Thus it is used in medicine, as a dietary supplement or slimming aid, usually as chromium(III) chloride, chromium(III) picolinate, chromium(III) polynicotinate or as an amino acid chelate, such as chromium(III) *D*-phenylalanine [48].

Besides these chromium is used for various other purpose like: as a catalyst; potassium dichromate used as titrating agent and as a mordant (*i.e.*, a fixing agent) for dyes in fabric; chromic acid prepared in situ by dissolving potassium dichromate in concentrated sulfuric acid is a powerful oxidizing agent and is a useful compound for cleaning laboratory glassware; chromium(IV) oxide (CrO_2) is used to manufacture magnetic tape, where its higher coercivity than iron oxide tapes gives better performance; used in well drilling muds as an anti-corrosive; chromium hexacarbonyl (Cr(CO)_6) is used as a gasoline additive; chromium boride (CrB) is used as a high-temperature electrical conductor [49-52].

1.2.1.3. Impact of hexavalent chromium in human health

Chromium as a metal is biological inert and does not produce toxic or other harmful effects in man or animal. Chromium (III) is an essential trace mineral required for sugar and lipid metabolism in humans and its deficiency may cause a disease called

chromium deficiency [48]. However, it is known that in an excessive concentration or long term exposure can result in skin allergies and cancer to human beings, inhibits the growth of certain algae and results in death of shellfish and fish [53]. Hexavalent chromium compound is highly toxic, considered as a priority pollutant because of its mutagenic and carcinogenic properties [54]. The chief health problems associated with chromium are related to Cr(VI) compounds exposure, which are irritation of eyes, skin and mucous, dermatitis resulting in skin ulceration, etc.

Hexavalent chromium compounds are genotoxic carcinogens. Chronic inhalation of hexavalent chromium compounds increases risk of lung cancer (lungs are especially vulnerable, followed by fine capillaries in kidneys and intestine). It was found that occupational exposure to hexavalent Cr compounds leads to a variety of clinical problems. Inhalation and retention of Cr(VI)-containing materials can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Skin contact of Cr(VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion [55, 56].

Chromium are toxic at different degrees at different stages of plant growth and development and also that the toxicity is concentration and medium dependent [57]. For plants, hexavalent chromium compounds are also more toxic than trivalent chromium compounds. A wheat plant was killed by 64 mg/l sodium dichromate [58]. Extensive reviews on the carcinogenicity of chromium have been published by government bodies, international organizations, and academic institutes and by individuals [59-61].

The toxic properties of chromates arise from the possibility of free diffusion across cell membranes and strong oxidative potential. The toxicological impact of Cr(VI) originates from the action of this form itself as an oxidizing agent, as well as from the formation of free radicals during the reduction of Cr(VI) to Cr(III) occurring inside the cell. Cr(III) formed there in a significant concentration can cause further adverse effects because of its high capability to coordinate various organic compounds resulting in inhibition of some metallo-enzyme systems [62].

Not only toxicity, but also the mobility and bioavailability of Cr, depend fundamentally on its chemical form. Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to sparingly soluble trivalent Cr species [63].

1.2.1.4. The chemistry of chromium(VI),d⁰

Chromium exists in several chemical forms displaying oxidation number from 0 to VI. Only two of them, trivalent and hexavalent Cr, are, however, stable enough to occur in the environment. Cr(IV) and Cr(V) form only unstable intermediates in reactions of trivalent and hexavalent oxidation states with oxidizing and reducing agents, respectively. The Cr(III) oxidation state is the most stable and considerable energy would be required to convert it to lower or higher states.

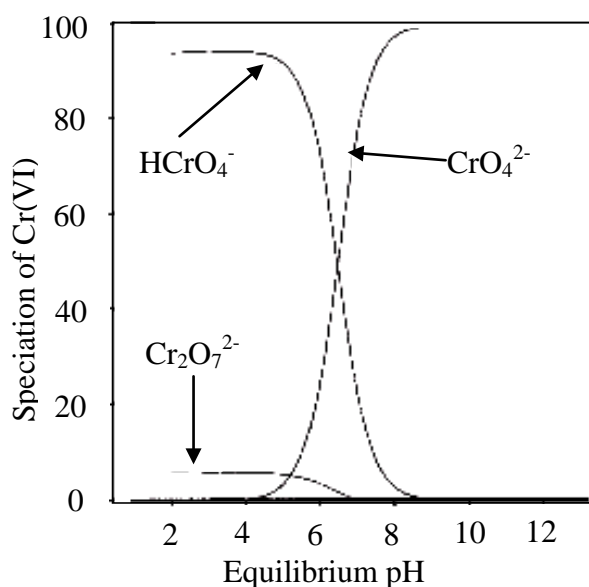
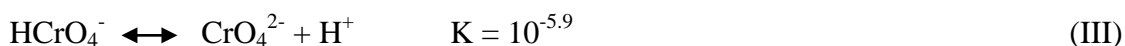
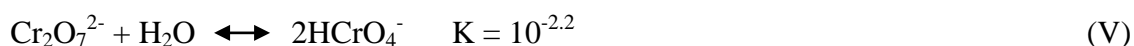


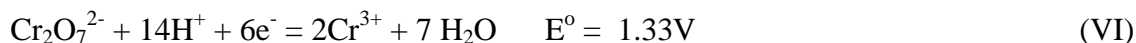
Fig. 1.4. Chemical equilibrium speciation of Cr(VI).

Cr(VI) forms several species, including Cr₂O₇²⁻, HCr₂O₇⁻, HCrO₄⁻, the relative proportions of which depend on both pH and total Cr(VI) concentration as shown in Fig. 1.4. [64]. In basic solutions above pH 6, it forms the tetrahedral yellow chromate ion CrO₄²⁻; between pH 1 and 6, HCrO₄⁻ and the orange red dichromate ion Cr₂O₇²⁻ are in equilibrium, but HCrO₄⁻ is the dominant species as shown in Fig.1.4. At pH values < 1 the main species is H₂CrO₄ [62]. The equilibria are the following:





Cr(VI) in acidic solution demonstrates a very high positive redox potential (E° within 1.33 and 1.38 V) which denotes that it is strongly oxidizing and unstable in the presence of electron donors [65-69].



The reduction of $\text{Cr}_2\text{O}_7^{2-}$ is accompanied by the H^+ consumption. Decrease in acidity decreases the redox potential. The chromate ion in basic solution, however, is much less oxidizing:



In more basic solution the reduction of CrO_4^{2-} generates OH^- against a gradient ($E^\circ = -0.13 \text{ V}$) [70]. This destabilizes Cr(III) relative to the Cr(VI) oxidation state results in a decrease of the redox potential with increased basicity (pH > 4 range).

The CrO_4^{2-} and HCrO_4^- ions are the most mobile forms of Cr in soils. They can be taken up by plants and easily leached out into the deeper soil layers causing ground and surface water pollution [71, 72].

1.2.1.5. Methods of chromium removal

Cr present in the atmosphere originates from anthropogenic sources which account for 60-70%, as well as from natural sources which account for the remaining 30-40% [73]. The main natural sources are volcanic eruptions, weathering of rock constitutes, wet precipitation and dry fallout from the atmosphere, and run-off from the terrestrial systems. The main human activities contributing to the Cr increase in the atmosphere are: metallurgical industries, refractory brick production, electroplating and tanning industries, from dyeing, sanitary landfill leaching, water cooling towers and other chemical industries [74]. Taking account of its harmful effects, many countries has implemented the maximum permissible level of Cr(VI) in water. The maximum level of Cr(VI) permitted in waste water as implemented by WHO is 0.5 mg/dm^3 [75] but effluents from such industries are usually higher than this. It is essential for such industries to treat their effluents so as to reduce Cr concentration to acceptable levels

before discharging into environment.

Various methods exist for the removal of Cr(VI) ion from waste water which include chemical reduction followed by precipitation, electrocoagulation, solvent extraction, reverse osmosis, ultrafiltration, biosorption/bioreduction, ion exchange, adsorption *etc.*

The most widely used method for waste water treatment is the chemical reduction using ferrous and/or other reducing agents, within subsequent pH adjustment to precipitate the Cr(III) ions [76]. The reducing agents commonly used for chromium wastes are sulphur dioxide, sodium sulphites, ferrous sulphates and various compounds containing ferrous ions [77-80]. The use of ferrous sulphate as reducing agent has the disadvantage that a large amount of $\text{Fe}(\text{OH})_3$ is formed at the stage of alkaline precipitation. In addition, this process introduces excessive amount of sulphate ions as a contaminant into waste water [81]. This process, apart from being economically expensive, have disadvantages such as high reagent and energy consumption, incomplete metal removal and generation of a large quantity of toxic waste sludge, which necessitates careful disposal in further steps. These disadvantages encouraged many studies on the use of electrocoagulation or electrochemical precipitation for the treatment of several industrial effluents [82,83]. This technique does not require supplementary addition of chemicals, completely remove Cr(VI) in low as well as high concentration and also reduces the volume of produced sludge [84-87]. Because of the relatively large capital investment and the expensive electricity supply, electrochemical water or wastewater technologies did not find worldwide application [88].

Ion exchange is the second most widely used method for Cr(VI) removal from aqueous solution [89]. It has several benefits like highly selective, limited pH tolerance, high regeneration. Currently used commercial ion exchange resins use huge amount of artificial plastics which, besides being expensive, are creating heavy load to the environment. Other methods that are used for Cr(VI) removal are solvent extraction, reverse osmosis, membrane filtration and ultrafiltration [90-94]. Nevertheless, many of these approaches are marginally cost-effective or difficult to implement in developing countries. Therefore, the need exists for a treatment strategy that is simple and robust and that addresses local resources and constraints. Adsorption is a versatile treatment

technique practiced widely in fine chemical and process industries for wastewater and waste gas treatment. The usefulness of the adsorption process lies in the operational simplicity and reuse potential of adsorbents during long-term applications. This solves the problems of sludge disposal and renders the system more economically viable, especially if low-cost adsorbents are used. Activated carbon, biomaterials, zeolites and different metallic oxide have been studied for Cr(VI) removal [95-98].

Treatment of heavy metal bearing wastewater using biomaterials is one of the most active research fields in recent years [99, 100]. Compared to conventional chemical treatment methods, biological treatment methods have many advantages, which include (i) low operation cost, (ii) steady performance, and (iii) easy recovery of some valuable metals [101]. Biological systems employing processes such as bio-reduction, bio-accumulation or biosorption using biomaterials have been extensively examined for their chromium removal abilities [102-104]. These systems offer potential alternatives to existing technologies used to remove Cr(VI) from wastewaters. The bio-reduction of Cr(VI) to Cr(III) was possible by biomaterials [104-106].

In spite of these remarkable advantages, there are still a few unsolved drawbacks to industrial applications of the biomaterials as organic reductant as well as adsorbent; (i) Reduction rate of Cr(VI) by the biomaterials were much slower than that by chemical reductant. Thus there is a need for searching new superior biomaterials capable of reducing Cr(VI) more fast even under weak acidic conditions ($>pH\ 4$). (ii) Natural biomaterials are generally biodegradable. It means that it can release soluble organic compounds into the aqueous phase during biosorption, which must be further removed before being discharged into the environment. (iii) Not only Cr(VI) but Cr(III) must be efficiently removed by same biomaterial, but optimum conditions for their removals are different from each other. As solution pH decreases, the removal efficiency and rate of Cr(VI) increase since protons participate in abiotic reduction reaction of Cr(VI) by biomaterial [107-105]. On the contrary, those of Cr(III) decrease with increasing the pH since protons inhibit adsorption reaction between cationic Cr(III) ions and negatively charged functional groups of biomaterial [107, 110]. To the best of our knowledge, nobody has ever seriously considered these un-negligible

problems until now. Researchers, however, have only focused on fundamental kinetic and/or equilibrium studies of Cr(VI) biosorption by unreported or less-researched biomaterials.

Activated carbon has undoubtedly been the most popular and widely used as adsorbent in wastewater treatment applications throughout the world. Among various adsorbent activated carbon is widely used because of its large specific area, multiple type of reactive surface sites, high chemical stability and easy availability. Activated carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels [111]. Activated carbon-based systems can remove a wide variety of toxic pollutants with very high removal efficiencies. For these reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewaters [112-114]. However, commercially available activated carbons may be expensive and, for this reason, any cheap material, with a high carbon content and low inorganics, can be used as a raw material for the production of activated carbon. The materials developed for this purpose range from agricultural waste products, biomass and various solid substances. Some examples are activated groundnut husk carbon [115], coconut husk and palm pressed fibers [116], coconut shell [117], wood and dust coal activated carbons [118, 119], coconut tree sawdust carbon [120], rice husk carbon [121], almond shell carbon [122], fly ash [123], and agricultural wastes [124] have been reported in literature. The past ten years has seen a developing interest in the preparation of low-cost adsorbents as alternatives to commercial activated carbon, which includes carbon developed from waste materials. The following table (Table 1.2.) gives a list of carbon materials prepared from low-cost biomaterials used for Cr(VI) recovery. But all those carbon preparation method are multistep and difficult which also use hazardous chemicals like KOH, H₂SO₄ *etc.* Beside this most of these papers made a mistake in analyzing chromium species in aqueous solution, resulting in incorrect elucidation of Cr(VI) biosorption; the Cr(VI) was removed from aqueous solution systems by ‘anionic adsorption’. However, it has been proved that Cr(VI) is easily reduced to Cr(III) by contact with organic materials under acidic conditions because of its high redox potential value (above +1.3V at standard condition). Therefore, it is strongly possible

that the mechanism of Cr(VI) removal by biomaterials or biomaterial-based activated carbons is not “anionic adsorption” but “adsorption-coupled reduction”. Thus, for researches of Cr(VI) adsorption, researchers have to analyze not only Cr(VI) but also total Cr in aqueous solution and to check the oxidation state of chromium bound on the biomaterials or activated carbons [125].

Table 1.2. Carbon used for Cr(VI) removal.

Biomaterial	Carbonization/activation process	pH	Chromium measurement	q (mg/g)	Refs.
Tamarind wood	Activation using ZnCl ₂ and carbonized under N ₂ atmosphere	6.5	Total Cr	28.019	[126]
Coconut shell	Activation using H ₂ SO ₄ acid and carbonized at 600 °C under inert atmosphere	2	Total Cr	32.61	[127]
Coconut shell fiber	Activation using H ₂ SO ₄ acid and carbonized at 600 °C under inert atmosphere	2	Total Cr	24.11	[127]
Green algae Ulva lactuca	Carbonized after H ₂ SO ₄ acid treatment	1	Cr(VI)	112.36	[128]
Fir wood	Activated with KOH and carbonized at 700 °C for 2 h under N ₂ atmosphere	3	Cr(VI)	180.3	[129]
Pine wood	Commercial activated carbon made by activation with H ₃ PO ₄	3	Cr(VI)	124.6	[129]
Terminalia arjuna nuts	Activation using ZnCl ₂ and carbonized under N ₂ atmosphere	1	Cr(VI)	28.43	[130]
Viscose rayon based AC cloth	Electrochemically reduced	4	Total Cr	3.8 mol/kg	[131]
Bael fruit shell	Carbonized after activation using H ₃ PO ₄	2	Total Cr	17.27 mg/g	[132]
Pomegranate husk	Carbonized after H ₂ SO ₄ acid treatment	1	Cr(VI)	35.2 mg/g	

Biomaterial	Carbonization/activation process	pH	Chromium measurement	q (mg/g)	Refs.
Cellulose	Activated using ZnCl ₂ and carbonized at 600 °C under N ₂ atmosphere	4	Cr(VI)	38 mg/g	[134]
Olive bagasse	Carbonized at 850 °C under N ₂ atmosphere	2	Cr(VI)	88.59 mg/g	[135]
Almond shell	Carbonized at 200 °C for 24 h after chemical activation using H ₂ SO ₄ (1:1 wt ratio)	1	Cr(VI)	190.3 mg/g	[136]
Date palm seed	Carbonized after H ₂ SO ₄ acid activation	1	Cr(VI)	120.48 mg/g	[137]
Ground nut husk	Carbonized after H ₂ SO ₄ acid activation	3	Total Cr	7 mg/g	[138]
Rubber wood sawdust	Carbonized at 400 °C for 1 h after H ₃ PO ₄ activation	2	Cr(VI)	64.44 mg/g	[139]
Casurina equisetifolia leaves	Carbonization after ZnCl ₂ activation	3	Cr(VI)	35 mg/g	[140]
Cow dung	Carbonization after H ₂ SO ₄ acid activation	3.4 2	Cr(VI)	1.90 mg/g	[141]
Rice husk	Carbonized after KOH activation	5	Cr(VI)	38.75 mg/g	[142]

1.3. E-waste and precious metals

1.3.1. E-waste

E-waste for short or waste electrical and electronic equipment (WEE) is the term used to describe old, end-of-life or discarded appliances using electricity [143,144]. It includes refrigerators, air conditioners, cell phones, personal stereos, and consumer electronics to computers which have been discarded by their users [145].

The use of electronic devices has proliferated in recent decades, and proportionately, the quantity of electronic devices, such as PCs, mobile telephones and entertainment electronics that are disposed of, is growing rapidly throughout the world. In 1994, it was estimated that approximately 20 million PCs (about 7 million tons) became obsolete. By 2004, this figure was to increase to over 100 million PCs.

Cumulatively, about 500 million PCs reached the end of their service lives between 1994 and 2003. Five hundred million PCs contain approximately 2,872,000 t of plastics, 718,000 t of lead, 1,363 t of cadmium and 287 t of mercury [145]. This fast growing waste stream is accelerating because the global market for PCs is far from saturation and the average lifespan of a PC is decreasing rapidly - for instance for CPUs from 4–6 years in 1997 to 2 years in 2005 [146]. PCs comprise only a fraction of all e-waste. Other constituents of e-waste are retired mobile phones and all kinds of portable electronic devices such as PDAs, MP3 players, computer games and peripherals [147].

When e-waste is disposed of or recycled without any controls, there are predictable negative impacts on the environment and human health. E-waste contains more than 1,000 different substances, many of which are toxic, such as lead, mercury, arsenic, cadmium, selenium, hexavalent chromium, and flame retardants that create dioxins emissions when burned. About 70 % of the heavy metals (mercury and cadmium) in US landfills come from electronic waste. Consumer electronics make up 40 % of the lead in landfills. These toxins can cause brain damage, allergic reactions and cancer [145].

E-waste contains considerable quantities of valuable materials such as precious metals. Early generation PCs used to contain up to 4 g of gold each; however this has decreased to about 1 g today. The value of ordinary metals contained in e-waste is also very high: 1 ton of e-waste contains up to 0.2 tons of copper, which can be sold for about 500 Euros at the current world price [148]. Recycling e-waste has the potential therefore to be an attractive business [149].

1.3.2. Precious metals

The term precious metal is used for gold, silver and platinum group metals (PGMs) where Platinum group metals (PGMs) consist of ruthenium (Ru), rhodium (Rh), palladium (Pa), osmium (Os), iridium (Ir) and platinum (Pt). These metals are extremely scarce compared to other metals due to their low abundance and the complex processes that are required to extract these metals from ores. In the last few years there has been a dramatic increase in the production of these technologically important metals. These metals are separated using the unique chemistry that the precious metals

exhibit. The first chemical characteristic exploited is their nobility, which refers to their extremely high inertia toward dissolution in media in which all other base metals dissolve. This is utilized during the selective leaching of base metals from the sulphide ores [150]. Other chemical characteristics that are exploited include their chloro-complexes, ligand substitution reactions, volatile tetroxides, ion-exchange reactions and oxidation states. All of these chemical characteristics are used not only to refine the PGMs from other metals but also to separate the different PGMs from one another [151].

A summary of the most important chlorocomplexes found in the leach solutions is given in the following table from which the mixed aquachloro and polynuclear species have been omitted.

Table 1.3. Common chlorospecies of the precious metal group [152].

Metal	Oxidation state	Major chlorospecies	Comments
Silver (Ag)	I	AgCl	Insoluble
		AgCl ₂ ⁻	High HCl Concentration
Gold (Au)	I	AuCl ₂ ⁻	Very stable
	III	AuCl ₄ ⁻	
Platinum (Pt)	II	PtCl ₄ ²⁻	Conversion IV to II slow
	IV	PtCl ₆ ²⁻	Most common species, kinetically inert
Palladium (Pd)	II	PdCl ₄ ²⁻	Most common
	IV	PdCl ₆ ²⁻	Conversion II to IV difficult
Iridium (Ir)	III	IrCl ₆ ³⁻	Both species stable and conversion IV to III easy
	IV	IrCl ₆ ²⁻	
Rhodium (Rh)	III	RhCl ₆ ³⁻	
Ruthenium (Ru)	III	RuCl ₆ ³⁻	Complex equilibria between III and IV, depending on redox potential and chloride concentration
	IV	RuCl ₆ ²⁻	

Metal	Oxidation state	Major chlorospecies	Comments
Osmium(Os)	III	OsCl ₆ ³⁻	Os(IV) more stable than Ru(IV)
	IV	OsCl ₆ ⁴⁻	

Steadily increasing demand for precious metals, especially platinum and palladium, has resulted in the scale-up of metal extraction and refining operations worldwide. This, combined with a technology shift towards aqueous/organic-based metal extraction, has resulted in a vast increase in the volumes of aqueous wastewater produced by such operations. In most cases, these wastewaters still contain appreciable amounts of valuable metal. Conventional methods for the removal of low concentrations of dissolved metal ions from wastewaters, such as solvent extraction, chemical precipitation and ion exchange, have significant disadvantages, which include incomplete metal removal, high capital costs, high reagent and/or energy requirements, and generation of toxic sludge or other waste products that require disposal [153, 154]. These disadvantages, together with the need for more economical and effective methods for the recovery of metals from wastewaters, have resulted in the development of alternative separation technologies.

By the same logic, the rising demand for platinum group metals (PGMs) in industry (*e.g.*, chemical catalysis, automotive catalysts), has prompted the research into new methods for their recovery from spent materials [155]. Pyrometallurgy has been investigated as a possible process [156]. However, this process is usually nonselective and there is a need for the development of alternative processes. The acidic treatment of spent catalysts or scrap materials (usually requiring hot aqua regia) leads to highly acidic solutions containing mixtures of base metals (BMs) and PGMs (including platinum, palladium, gold, rhodium, iridium.). Recently, a more benign leaching method, using more dilute aqua regia and microwave-accelerated leaching was described which increases the attractiveness of hydrometallurgical processing [157]. However, the separation of PGMs from BMs in the mixtures is a strategic challenge; and the selective separation of different precious metals is the focus of much research [158-163]. Most studies focusing on PGMs separation have been dedicated to the design of solvent extraction processes and to the synthesis and testing of conventional

ion exchange and chelating resins [164-170]. However, an increasing interest exists for the use of alternative materials, such as materials of biological origin for the recovery of metals [171-173]. These materials are abundant and environmentally friendly.

1.4. Objectives of the present study

The short term objectives of the study are:

1. To explore the scope of agricultural waste like rice husk, barley straw and wheat straw as raw materials for preparation of porous carbon.
2. To explore a simple single step carbonization process for generation of porous carbon from agricultural waste materials.
3. To prepare and characterize the prepared porous carbon.
4. To determine the adsorption behavior and to estimate the maximum adsorption capacity of these porous carbons to various metal ions like Cr(VI), Pt(IV), Au(III), and Pd(II).
5. To modify and characterize the porous carbon materials by simple oxidation method and to evaluate the modified carbon by Cr(III) adsorption.
6. To suggest ways to separate toxic metals and recover precious metals from e-waste by using the prepared porous carbon.

The long term objectives of the study are:

1. To establish agrowaste as a useful biomass in the form of porous carbon and substitute the expensive and synthetic materials in the preparation of adsorbent.
2. To contribute to a sustainable society through effective separation and recovery technology
3. To contribute to the protection of environment and improvement in human health.

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Preparation and characterization of carbon from agrowaste

A study on the preparation of carbon from agrowaste like rice husk, barley straw and wheat straw involving a single step carbonization process have been examined. Experiments have been carried out at different carbonization temperature from 600 – 1000°C at a heating rate of 5 °C min⁻¹ and 1 h carbonization time. The influence of the carbonization temperature on the surface area of the carbons was evaluated. The specific surface area of CRH, CBS as well as CWS increases by increasing the carbonization temperature from 600-800°C and reaches a maximum value of 348,792 and 700 m²/g, respectively, at 800°C. On further increasing the temperature, the surface area decreases. These experimental results indicated the potential use of agrowaste like barley straw and wheat straw as a precursor in the porous carbon preparation process, thus representing an economically promising material.

2.1. INTRODUCTION

Activated carbons have been widely used as industrial adsorbents for separation, purification, and recovery process due to their extended surface area, high adsorption capacity, microporous structure and special surface reactivity [1-4].

Carbonization of carbon containing raw materials is the prerequisite step for preparation of carbon but the porosities of carbon is not sufficiently developed to meet the need of the fields such as environmental protection. Thus, the development of the active carbon with high specific surface area is necessary. Thus, carbonization is simultaneously followed by “physical” activation, consists of heating at a relatively high temperature under a carbon gasification reactant (H₂O or CO₂) or “chemical” activation, consists of heating at a relatively lower temperature with the addition of chemical reagents (*e.g.*, KOH, H₃PO₄, ZnCl₂) or combination of both. Consequently, the preparation procedure of highly porous carbon becomes difficult and expensive [5].

During the last two decades, the research and development of active carbons process has been done enormously. The active carbon with specific surface area as high as 3000 m²/g has also been prepared by using potassium hydroxide as activating reagent [6]. Although the active carbons produced are of high specific surface area and of generally good properties, they are all made from coal, petroleum coke or a mixture and by using multistep preparation process which also use expensive and hazardous chemicals [7].

Considerable quantities of agricultural by-products results from the annual harvesting and processing of various agricultural crops grown around the world. The amount of such agro-waste is far in excess of any local uses and thus poses a disposal problem. More recently, these by-products have been shown to have potential as precursor materials in the manufacture of activated carbons, usually with comparable adsorption capacity with that of commercial activated carbons [8-11]. Proper utilization of agricultural by-products is very important for the national economy. It would not only help in solving the disposal problem, but would also help in reducing the shortages with respect to several materials. The use of such agrowaste in carbon preparation can help in the reduction of the cost in carbon preparation and most importantly would provide a potentially inexpensive alternative to existing, extensively used, commercially available activated carbons, especially coal-based carbons in many industrial applications.

Hence, the aim of this study was to evaluate the feasibility of the agrowaste like wheat straw, barley straw and rice husk as a precursor for porous carbon production, by using very simple single step preparation method. The influence of carbonization temperature on the carbon specific surface area was evaluated.

2.2. Experimental

2.2.1. Preparation of carbonized materials. Carbon from rice husk, wheat straw and barley straw was prepared by employing very simple method of carbonization without using any activation process. Rice husk, wheat straw and barley straw were separately

ground in an alumina vibration mill. The resulting samples were then put in an alumina crucible with an alumina cover. This crucible was put in a larger alumina crucible and covered with graphite powder and capped with an alumina cover in order to prevent oxidation. The crucible set was put into a furnace with a heating rate of 5 °C/min and then heated up to the carbonization temperature. The straw was carbonized at different carbonization temperatures (600, 700, 800, 900 and 1000°C) for 1 h. After 1 h the electric furnace was automatically switched off. The door of the electric furnace was not opened until cooling to room temperature had taken place. This will prevent oxidation of carbon samples in air at high temperature. The obtained carbonized material was ground again, washed with distilled water and dried in an oven at 50°C for 24 h and used for the experiments under the names of carbonized rice husk (CRHxxx), carbonized wheat straw (CWSxxx) and carbonized barley straw (CBSxxx).

*Where, 'xxx' corresponds to the carbonization temperature.

The graphite powder used during carbonization can be reused. Since the only one that takes cost in this process is electricity, this process is comparatively cheaper and convenient in comparison to other carbon preparation process.

2.2.2. Surface characterization. Physical gas adsorption is an extensively used technique in the characterization of porous materials which accurately determines the surface area, pore volume and pore size distribution. The adsorption of such gases as N₂, Ar and CO₂ is frequently used for this purpose. In this case N₂ adsorption at 77 K was carried out using a Belsorp 18PLUS-SP (BEL. JAPAN. INC.). Before measuring the adsorption of N₂, the sample was subjected to degassing for 3 h at 300°C to a final pressure of 0.1 Pa. The N₂ adsorption-desorption isotherms were analyzed to characterize the nature of the pores. BET-Plots and t-Plots were analyzed to calculate the specific surface area and average pore diameter. The classical pore size model developed by Barret, Joyner and Halande (BJH) was used for the pore size distribution calculation.

Thermogravimetric analysis was performed on the carbon materials using a TG/DTA 6300 (Seiko Instruments Inc.). About 5 mgs of each sample were heated from 10 to 1000°C at a heating rate of 10°C/min. The result provided TG plots.

The pH values required to give zero net surface charge, designated the point of zero charge (PZC), of the samples, CRH800, CBS800 and CWS800, were measured by a mass titration method [12]. Three solutions with different initial pH values were prepared using HNO₃ and NaOH, wherein NaNO₃ was used as the background electrolyte. For each initial pH value, six conical flasks were filled with 25 ml of the solution and different amounts of the carbon sample were added so as to make the solid fraction 0.05%, 0.1%, 0.5%, 1%, 5% and 10% respectively. The mixture was shaken for 24 h and the equilibrium pH value was measured.

2.3. Results and discussion

2.3.1. Effect of carbonization temperature. The % yield of carbonized materials is defined as the ratio of the mass of carbonized products upon the mass of the raw materials used multiplied by 100. Carbonization at different temperature has been performed in order to determine the temperature at which the % yield as well as the specific surface area was high. Table 2.1. shows that the yield of carbonized materials decreases as the carbonization temperature increases from 600 to 1000°C. This is attributed to the removal of volatile matters resulting from the decomposition of cellulose, hemicellulose *etc.* But the decrease in % yield is very less, only about 1% with every 100°C increase in carbonization temperature.

Table 2.1. Effect of carbonization temperature on % yield of porous carbon.

Carbonization temperature	Yield (%)		
	CRH	CBS	CWS
600°C	34.68	29.62	29.21
700°C	33.55	28.16	27.98
800°C	32.45	27.27	27.01
900°C	30.08	24.72	25.05
1000°C	29.02	22.59	23.02

Table 2.2. shows the BET area and t-plot area of carbons prepared at different carbonization temperatures. BET area is the minimum possible specific surface area where as t-plot area is the maximum possible specific surface area. Thus mean of these two specific surface area has been considered as the actual specific surface area for the carbon. The effect of carbonization temperature on specific surface area keeping the heating rate at $5^{\circ}\text{C min}^{-1}$ is shown in Fig. 2.1. The specific surface area of CRH, CBS and CWS increases with increasing temperature from 600°C to 800°C and reaches a maximum value at 800°C . It slightly decreases with a further increase in the carbonization temperature from 800 to 1000°C . The maximum specific surface area was 348, 792 and $700\text{ m}^2/\text{g}$ for CRH800, CBS800 and CWS800, respectively. It can be observed that highly porous carbon with very high specific surface area like that of commercially available activated carbon can be obtained from barley straw and wheat straw by applying very simple method of carbonization without using any activation process. The increase in the specific surface area from $600\text{-}800^{\circ}\text{C}$ is due to the removal of volatile substances while the decrease in surface area at higher temperature is attributed to the widening and destruction of pores due to excessive heating as well as accessibility to adsorbate gases decreases as cross-linking of carbon atoms reduces space between atoms and essentially closes off porosity to an adsorptive gas. Thus 800°C is the optimum carbonization temperature since the specific surface area is maximum and the yield % is high enough at 800°C .

Table 2.2. Specific surface area of porous carbon as measured by BELLSORP.

Carbonization temperature	Specific surface area (m ² /g)								
	CRH			CBS			CWS		
	BET	t-Plot	Mean	BET	t-Plot	Mean	BET	t-Plot	Mean
600 °C	247	303	275	424	547	485	242	308	275
700 °C	290	350	320	553	688	620	283	377	330
800 °C	322	374	348	723	861	792	634	766	700
900 °C	239	281	260	680	835	757	436	554	495
1000 °C	46	57	51	604	776	690	363	445	404

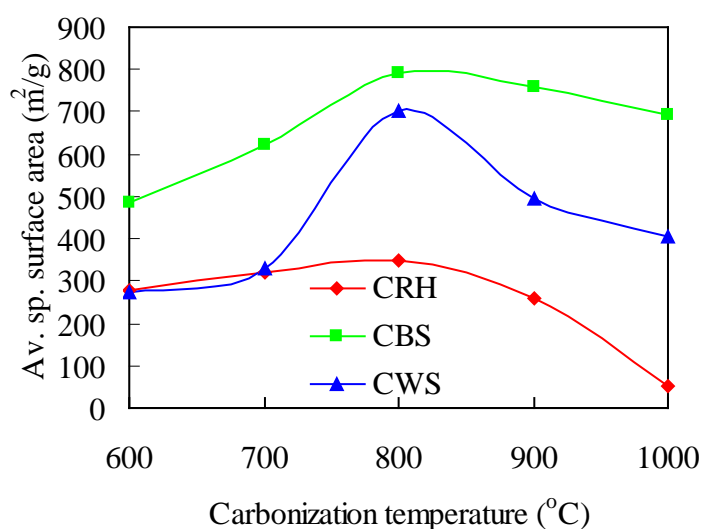


Fig. 2.1. Effect of carbonization temperature on average specific surface area of carbon.

The N₂ adsorption-desorption isotherms of CRH800, CBS800 and CWS800 are shown in Fig. 2.2. The adsorption isotherms for all samples investigated were primarily of Type I, a characteristic of microporous materials. However, the small hysteresis loop in the adsorption-desorption isotherms indicates the existence of mesopores. When a solid contains very fine micropores, the potential force field from the neighboring walls

of the pores will overlap causing an increase in the interaction energy between the solid surface and the gas molecules. This will result in an increase in adsorption, especially at low relative pressures causing complete filling of the pores at quite a low relative pressure, giving rise to a Type I isotherm. These isotherms are thus characterized by a plateau exhibiting a small amount of adsorption at higher relative pressures. The pores are too narrow to accommodate more than a single molecular layer, and so the Type I isotherms do not increase continuously [13].

In the presence of mesopores, capillary condensation will occur during adsorption and is preceded by a metastable fluid state (“cylindrical meniscus”), while capillary evaporation during desorption occurs via a hemispherical meniscus, separating the vapor and the capillary condensed phase, which will result in hysteresis, since mesopores are filled at higher pressure and emptied at lower pressure [14].

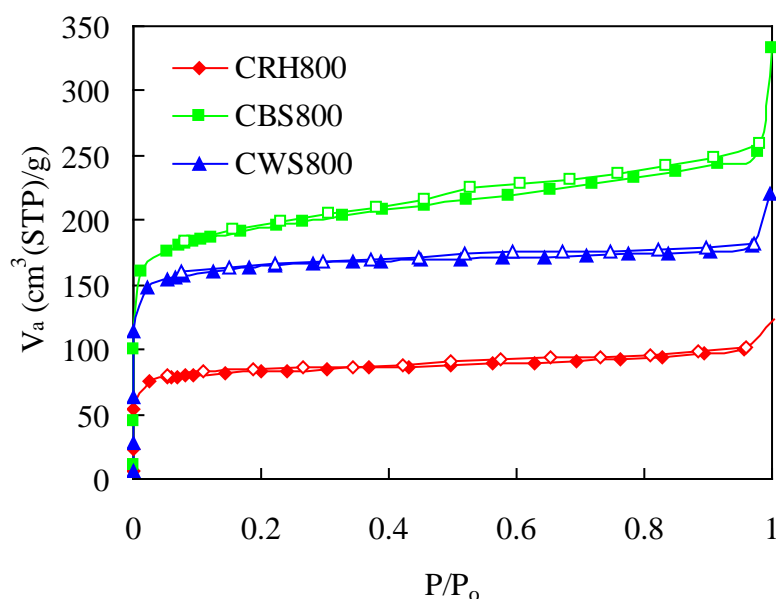


Fig. 2.2. Nitrogen adsorption (closed symbol) and desorption (open symbol) isotherms for carbons. V_a = Volume of N_2 adsorbed; P/P_0 = Partial pressure of N_2 .

Figure 2.3. shows the pore size distribution of CRH800, CBS800 and CWS800. This figure clearly shows that the majority of pore in all carbons prepared here are microporous having pore size less than 2 nm. The figure also shows that the volume of

pore in microporous region is highest in CBS800 followed by CWS800 and CRH800.

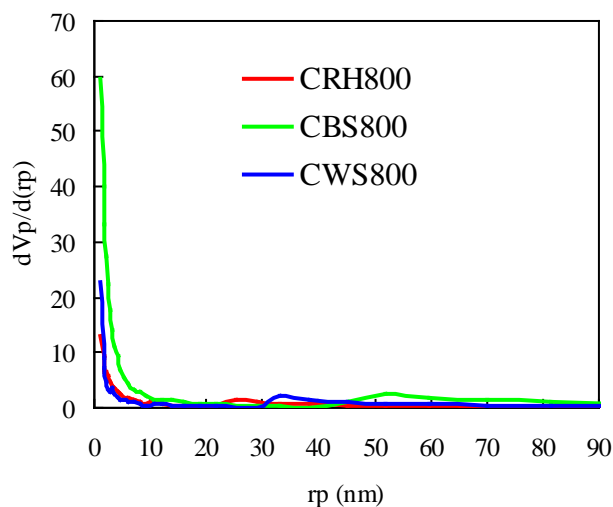


Fig. 2.3. Pore size distribution.

The X-ray diffraction analysis (figure omitted for brevity) of the porous carbons did not show any sharp peaks, thereby indicating the amorphous nature of the carbons prepared from. The appearance of a broad peak centered at $2\theta = 22.5$, however, indicated the existence of amorphous silica in the sample.

Table 2.3 lists the porosity of pores as determined from nitrogen adsorption isotherms.

Table 2.3. Pososity of carbons as determined by nitrogen adsorption.

Carbon	Sp. surface area (m^2/g)	Pore volume V_p (cm^3/g)	Average pore diameter
CRH800	348	0.06	2.24 nm
CWS800	700	0.12	2.03 nm
CBS800	792	0.20	2.52 nm

2.3.2. Thermogravimetric analysis (TGA). Figure 2.4. shows the thermogravimetric plot of CRH800, CBS800 and CWS800. In all types of carbon, weight loss commences quite early as shown close to 70°C, indicating water loss. Then after weight loss in the lower temperature range is not marked but a sharp weight loss occurs near 500°C indicating decomposition of carbon materials forming CO₂ and CO. The unburned wt % determines the ash content of carbon which can not be burnt off. Fig.2.4. shows that the ash content of CRH800 is quite high whereas the ash content of CWS800 and CBS800 is negligible which was 36, 7 and 7 wt% respectively. The ash content is mainly due to silica as also confirmed by XRD analysis.

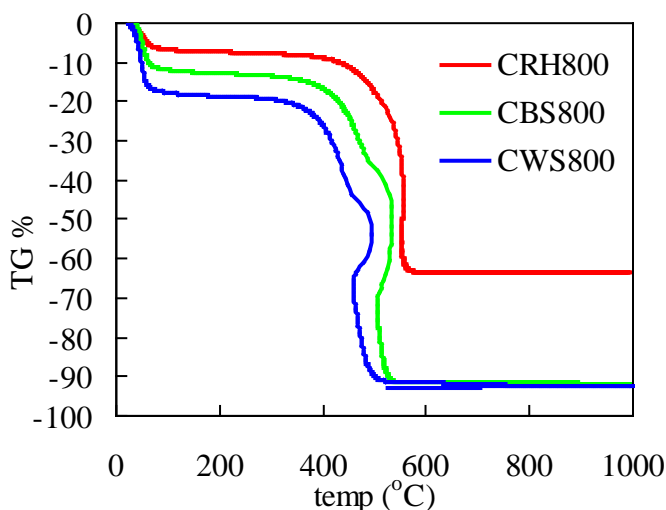


Fig. 2.4. Thermogravimetric plot

2.3.3. Potential of zero charge (PZC). Figure 2.5. shows the mass titration curves of CRH800, CBS800 and CWS800. These plots show the change in pH value as a function of the mass fraction of carbonized material in the solution (wt/v%). The plot exhibits a plateau and the PZC was evaluated as the average of three asymptotic pH values. The PZCs of CRH800, CWS800 and CBS800 were evaluated as 8.0, 9.0 and 9.2, respectively. The carbon surface is positively charged below this pH and negatively charged above it. The PZC values shows the possibility of anionic adsorption on the carbon surface at acidic pH range thus this carbon can be used for recovery of Cr(VI), Au(III), Pd(II), Pt(IV) *etc.*, which exist in anionic state in the industrial solution.

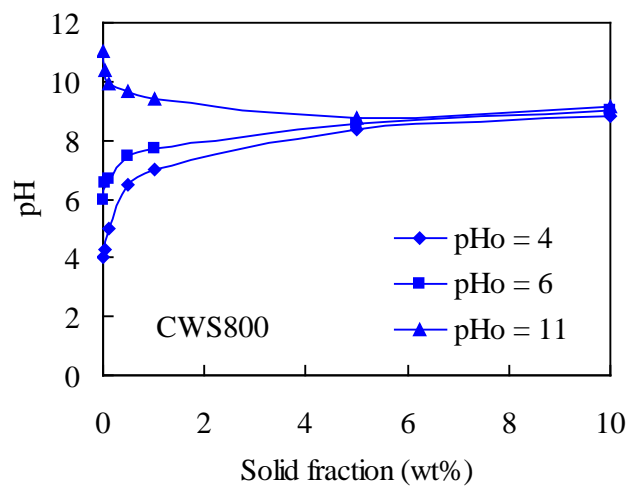
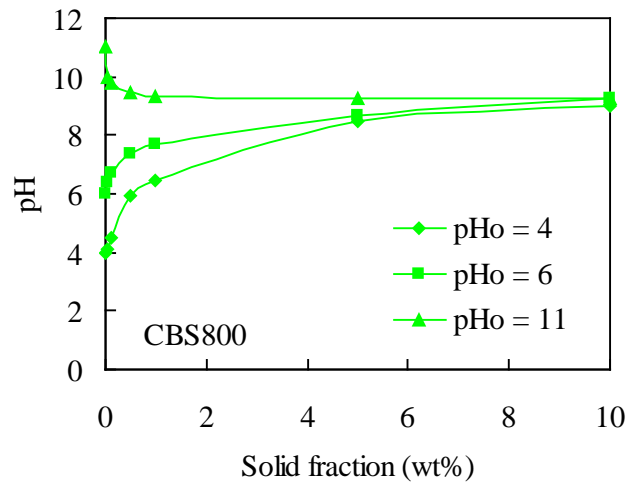
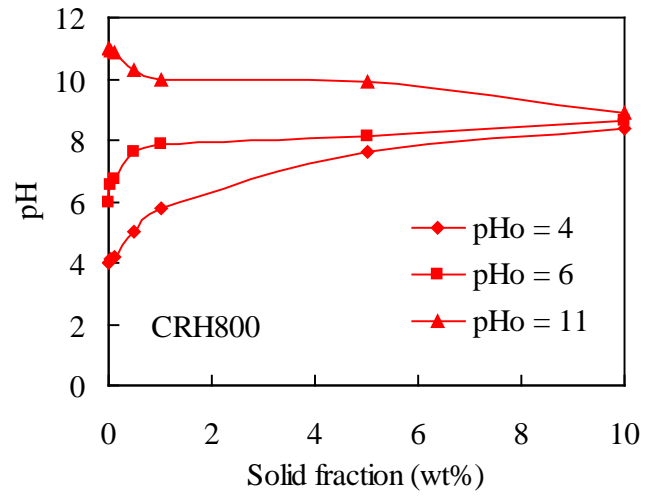


Figure 2.5. Mass titration curves of CRH800, CBS800 and CWS800 where pH_o stands for initial pH.

2.4. Conclusions

High surface area porous carbons are prepared by simple single step carbonization method. At 800°C carbonization temperature the carbon produced has high specific surface area as well as good % yield thus it is the optimum carbonization temperature. Wheat and barley straws are found to be good raw materials in comparison to rice husk because of generation of porous carbon with low ash content and high specific surface area. The carbon prepared is mainly microporous with positively charged surface at acidic pH. Thus it can be good adsorbent for metal ion such as Cr(VI), Au(III), Pt(IV) and Pd(II) which exist in anionic form in aqueous solution.

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Evaluation of wheat straw and barley straw carbon for Cr(VI) adsorption

The present study deals with the adsorption of Cr(VI) on carbonized wheat straw (CWS) and barley straw (CBS). Carbon materials, prepared at different carbonization temperatures, were investigated for the adsorptive removal of Cr(VI). These carbonized materials prepared from agro-waste were found to have a high affinity for chromium as represented by very high adsorption capacities of 1.67 and 1.68 mol/kg for wheat and barley straws carbonized at 800°C, respectively, at pH 2. Equilibrium was reached within 1 h of contact time which suggests high efficiency of the carbonized materials for Cr(VI) removal.

3.1. Introduction

Chromium is a redox active element, with oxidation states from -2 to +6, but only the +3 and +6 states are prevalent in aqueous solution [1]. Hexavalent chromium is highly toxic pollutant [2] generated from many industrial processes like manufacturing pigment in paints, inks, and plastics, as an anti-corrosion agent in protective coatings, and in chrome plating, leather tanning *etc.* [3]. Considering its hazardous risks for human health, the treatment of industrial effluents to reduce or remove the pollutant before discharge into the environment becomes inevitable.

A wide range of physical and chemical processes is available for the removal of Cr(VI) from water, such as electrochemical precipitation [4], ultrafiltration [5], ion exchange [6] and adsorption [7]. The adsorption process is one of the efficient methods for chromium removal [8] due to its clean operation and complete removal of heavy

metal ions even from dilute solutions. Activated carbon is the most widely used adsorbent for this purpose because of its large surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. However, commercially available activated carbons are expensive, which has led to a search for cheaper substitutes. Consequently, a number of low-cost adsorbents have been prepared for Cr removal. These include those prepared from rice husks [9], sawdust [10], apricot stones [11], cow dung [12] *etc.* However, since the adsorption capacities of these carbon materials are unsatisfactory or their preparation is not easy, new adsorbents are still under development.

In the present work, porous carbon materials was prepared from low-cost agro-waste like barley straw and wheat straw for the first time by applying very simple method of carbonization without using any activation process. Thus prepared carbon have been tried as adsorbents for the removal of Cr(VI) from aqueous solutions.

3.2.Experimental

3.2.1. Preparation of carbonized materials. Carbon from wheat and barley straws was prepared by carbonization process as discussed in section 2.2.1. of Chapter 2.

3.2.2. Surface characterization. The specific surface areas and average pore diameters of the carbonized materials were measured by using a Belsorp 18PLUS-SP (BEL. JAPAN INC.). The surface structures were observed by means of a scanning electron microscope (JEOLJSM-5510LV SEM).

The pH values required to give zero net surface charge, designated the point of zero charge (PZC), of the samples, CBS800 and CWS800, were measured by a mass titration method [13].

3.2.3. Preparation of synthetic test solutions. Aqueous solutions of Cr(VI) were prepared by dissolving analytical grade K_2CrO_4 in 0.1 M hydrochloric acid. The initial pH value of the solution was adjusted by adding small amounts of a 5 M ($M = \text{mol dm}^{-3}$) hydrochloric acid solution or a 5 M sodium hydroxide solution.

3.2.4. Adsorption tests. The adsorption tests were carried out in batch mode by adding 25 mg of adsorbent to 15 ml of a Cr(VI) solution in a 50 ml conical flask. The mixture was shaken in a thermostated shaker at 30°C and 150 rpm. The shaking time was 24 h for all experiments except for the kinetic experiments. After 24 h, the suspended mixture was filtered through a filter paper. The filtrate was analyzed for its chromium content as described in the subsequent section and the equilibrium pH was measured using an ORION model 720A pH meter. The pH of the solution mentioned hereafter is equilibrium pH of the solution. All the experiments were conducted in duplicate and mean values are reported in this thesis. The maximum deviation observed was less than 5%.

3.2.5. Chromium analysis. Park *et al.* [14] mentioned that Cr(VI) removal by bio-materials based carbon is not “anionic adsorption” but “adsorption-coupled reduction”. Thus researchers have to analyze not only Cr(VI) but also total Cr in aqueous solution and to check the oxidation state of chromium bound on the carbons. Considering this facts the final chromium content of the filtrate was determined using a Shimadzu model ICPS-8100 ICP/AES spectrometer which measures the total chromium ion {Cr(VI) + Cr(III)} present in the aqueous solution. Electron spin resonance (ESR) measurements by using X-band ESR spectrometer (JEOL JES TE-300) was also done for the CBS800 and CWS800 after Cr adsorption to determine the oxidation states of adsorbed Cr. To study the actual mechanism of adsorption, in case of kinetic experiments, the Cr(VI) concentration was also measured by the diphenylcarbazide method using a Hitachi model U-3310 UV visible spectrophotometer [15]. The difference between the total Cr concentration and the Cr(VI) concentration gives the concentration of Cr(III) present in the test solution.

3.3. Results and discussion

3.3.1. Surface characterization. The effect of carbonization temperature on specific surface area is discussed in section 2.3.1. Samples of powdered CWS800 and CBS800 were observed using a scanning electron microscope at 1000 X magnification as shown in Fig. 3.1., from which it is observed that both have irregular structures.

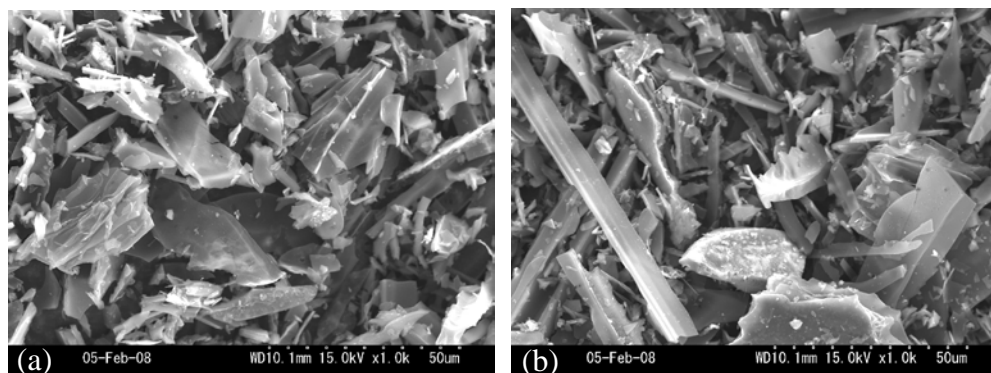


Fig. 3.1. SEM images of (a) CBS800 and (b) CWS800.

The result of mass titration is discussed in section 2.3.3. The results shows that the surface of CWS800 and CBS800 is positively charged below pH 9.0 and 9.2, respectively and negatively charged above it.

3.3.2. Adsorption tests

3.3.2.1. Effect of carbonization temperature. The effect of carbonization temperature on Cr(VI) adsorption was tested at pH 2 ± 0.1 as shown in Fig. 3.2. Maximum adsorption of Cr(VI) was observed at 800°C for both types of straw, which appears to correspond to the surface area of these carbonized materials as shown in Fig. 3.2. Figure 3.3 shows the relationship between surface area and the amount of adsorption of Cr(VI) at pH 2 ± 0.1 , where a good linear relationship is observed. Since both carbonized materials exhibited maximum adsorption at the carbonization temperature of 800°C, all other experiments were carried out by employing CBS800 and CWS800.

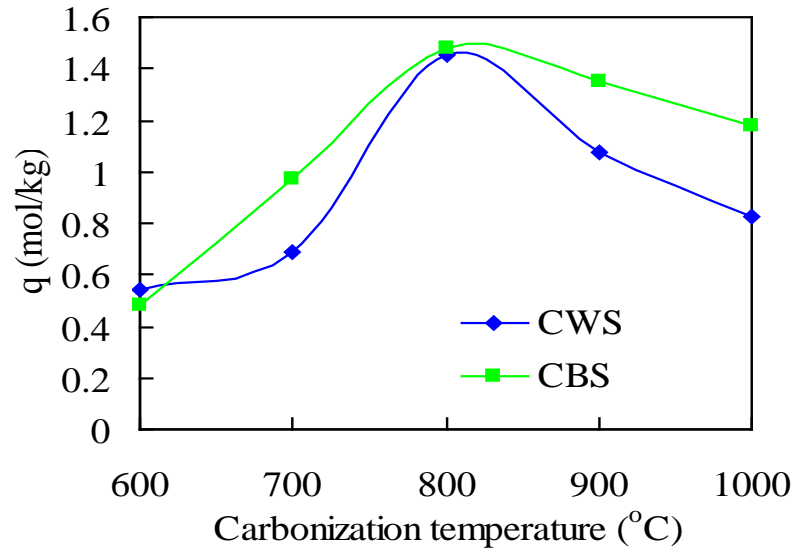


Fig. 3.2. Effect of carbonization temperature on Cr(VI) adsorption on CBS and CWS. Weight of adsorbent= 25 mg; Volume of Cr(VI) solution= 15 ml; Concentration of chromium (VI)= 200 ppm; Shaking time=24 h; $pH_{eq} = 2 \pm 0.1$.

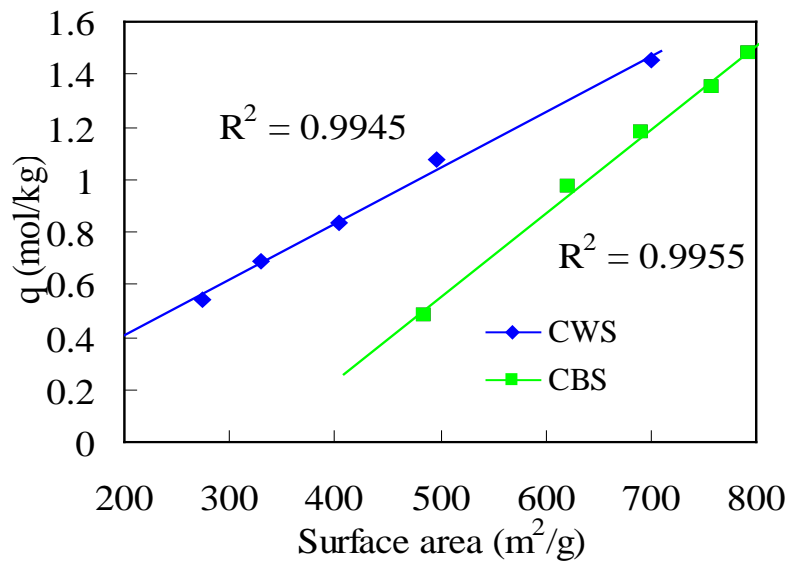


Fig. 3.3. Effect of surface area on adsorption of Cr(VI). Weight of adsorbent= 25 mg; Volume of Cr(VI) solution= 15 ml; Concentration of chromium (VI)= 200 ppm; Shaking time=24 h; $pH_{eq} = 2 \pm 0.1$.

3.3.2.2. Effect of pH. The distribution of anionic species of Cr(VI) and the surface properties of the adsorbents used to remove Cr(VI) ions are strongly dependent on the solution pH. The PZC analysis showed that the surfaces of CWS800 and CBS800 are

positively charged at pH values lower than 9. Cr (VI) exists in the form of HCrO_4^- and CrO_4^{2-} ions in aqueous solution among which the HCrO_4^- ion is stable and dominant at pH values lower than 5 [16]. Consequently, the adsorption mechanism of the Cr(VI) ion on the adsorbents is interpreted in terms of electrostatic interaction between the positively charged carbon surface and the negatively charged species of Cr(VI).

Fig. 3.4. shows the adsorption capacity of Cr(VI) on CWS800 and CBS800 at different equilibrium pH values. For both adsorbents, maximum adsorption is observed at $\text{pH } 2 \pm 0.1$, while at lower and higher pH values the adsorption capacity decreases. The decrease in adsorption of Cr(VI) ion at higher pH values is inferred to be due to the competition between the anionic chromium species (HCrO_4^- and CrO_4^{2-}) and OH^- ions for the active sites on the adsorbent. The decrease in adsorption at pH values lower than 2 is attributed to the reduction of Cr(VI) to Cr(III), which will be discussed later.

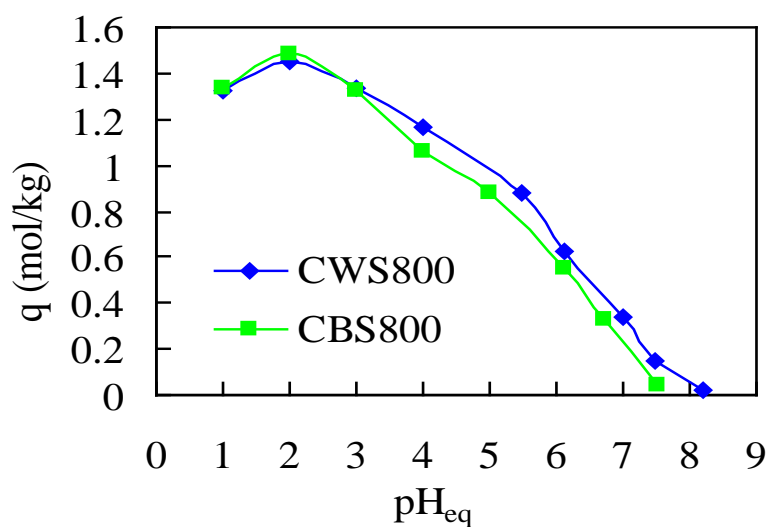


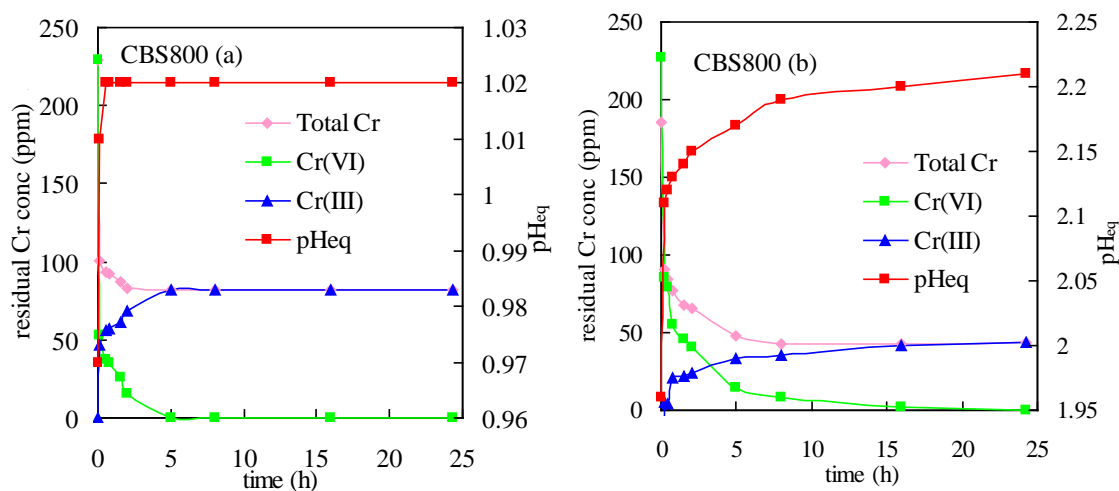
Fig. 3.4. Effect of pH on adsorption of Cr on CBS800 and CWS800 from Cr(VI) solution. Weight of adsorbent= 25 mg; Volume of Cr(VI) solution= 15 ml; Chromium(VI) concentration= 200 ppm; Shaking time=24 h.

3.3.2.3. Effect of contact time. Figures 3.5 (a), 3.5 (b) and 3.5 (c) shows the rate of change of the concentrations of Cr(VI) and Cr(III) as well as total chromium in the adsorption on CBS800 at three different initial pH 0.97, 1.96 and 2.51, respectively. The Cr(VI) concentration sharply decreased within 10 min in all cases and gradually

decreases later attending equilibrium within 5 h of contact time. The concentration of Cr(III), which was not initially present in the aqueous solution, increased as that of Cr(VI) reduced. This result indicates that some Cr(VI) was reduced to Cr(III) after coming in contact with the carbon surface. Since the carbon surface is composed of an electron rich graphene-like layer structure [17], Cr(VI), which is adsorbed on the carbon surface in the form of an anionic species, gains electrons from the electron rich graphene structure and is thus reduced to Cr(III) according to the following reaction.



After reduction, Cr^{3+} is desorbed due to electronic repulsion from the positively charged carbon surface. Comparison of Figures 3.5 (a), 3.5 (b) and 3.5 (c) clearly shows that the reduction rate of Cr(VI) is higher at lower pH and decreases on increasing pH, which can be interpreted by the effect of the hydrogen ion on the reduction of Cr(VI) as suggested by the above reaction.



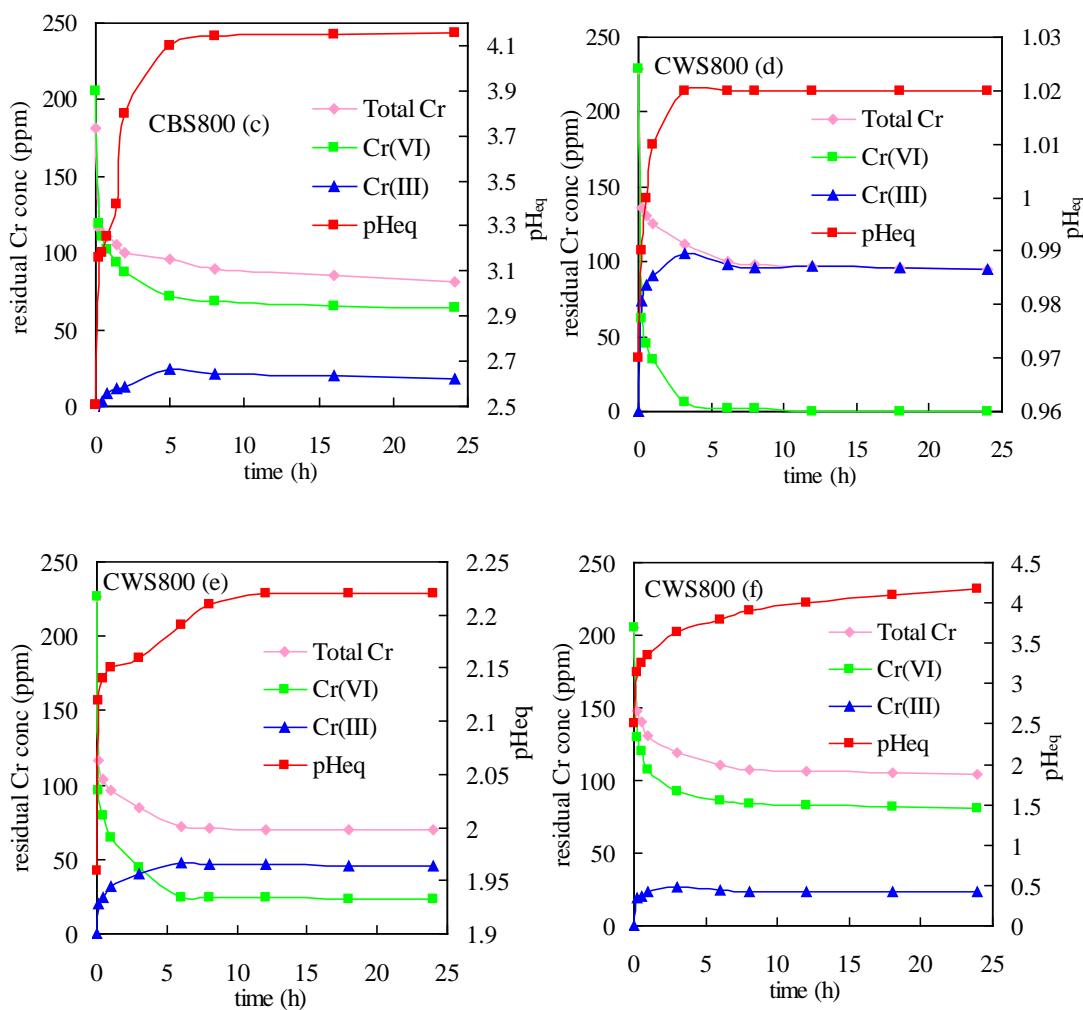


Fig. 3.5. Rate of change of pH, Cr(VI) and Cr(III) concentrations. Weight of adsorbent= 25 mg; Volume of Cr(VI) solution= 15 ml; Initial Cr(VI) concentration= 200 ppm.

To observe the effect of H^+ ion concentration on Cr(VI) reduction, the pH change of the solution was also monitored as a function of time. It was observed that the solution pH increased abruptly from from 0.97 to 1.02, 1.96 to 2.22 and 2.51 to 4.17 in case of CWS800 and 0.97 to 1.02, 1.96 to 2.21 and 2.51 to 4.16 in case of CBS800 as shown in Figures 3.5. The increase of the solution pH was likely to be related to the use of H^+ ion for reduction of Cr(VI) to Cr(III). Table 3.1. shows the ratio of the amount of hydrogen ion depletion to the amount of Cr(III) generated after reduction of Cr(VI) at different pH. The ratio was approximately 7 at all pH studied which proves that reduction of Cr(VI) occur as shown in equation 1 according to which 7 mole of H^+ ion is used for reduction of 1 mole of Cr(VI) to generate one mole of Cr(III). The increase of pH with disappearance of Cr(VI) ion and the appearance of Cr(III) ion initially not

present in the solution conclude that the adsorption-coupled reduction mechanism contributed to the removal of Cr(VI) from aqueous solution.

Table 3.1. Ratio of the amount of Hydrogen ion depletion to the amount of Cr(VI) reduced.

Adsorbent	pH _{eq}	Decrease in [H ⁺] ($\Delta[H^+]$)	Reduced Cr(VI) ([CrIII])	$\Delta[H^+]/[CrIII]$
CBS800	1.02	0.0116M	0.0016M	7.25
	2.21	0.0049M	0.0008M	6.13
	4.16	0.0030M	0.0004M	7.50
CWS800	1.02	0.0116M	0.0017M	6.82
	2.22	0.0049M	0.0008M	6.17
	4.17	0.0030M	0.0004M	6.86

3.3.2.4. Adsorption isotherms of chromium. Figure 3.6. shows the adsorption isotherms for chromium on CBS800 and CWS800 at pH 1 and 2. The amount of adsorption increases with increasing chromium concentration in its low concentration region and tends to approach a constant value in the high concentration region, exhibiting the typical Langmuir type adsorption.

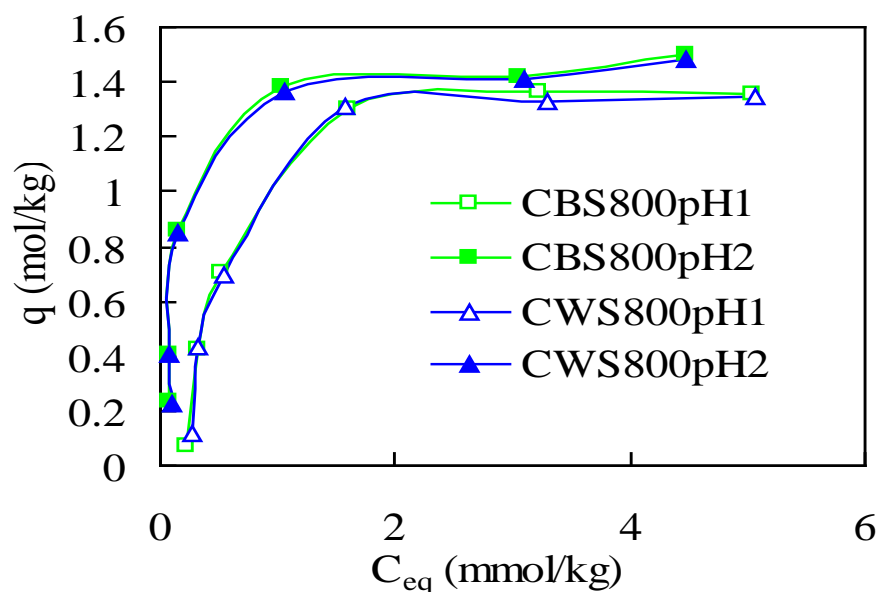


Fig. 3.6. Effect of equilibrium chromium concentration on its removal by CBS800 and CWS800. Weight of adsorbent= 25 mg; Volume of Cr(VI) solution= 15 ml; Shaking time=24 h.

Consequently, the adsorption isotherm data was fitted with the following Langmuir equation.

$$1/q_e = 1/(C_e \cdot \theta \cdot b) + 1/\theta \quad (2)$$

where:

q_e = amount adsorbed at equilibrium (mol/kg)

C_e = equilibrium Cr concentration in solution (mol/L)

θ and b are Langmuir isotherm constants, which are related to adsorption capacity and affinity of adsorption, respectively, were determined from the slope and intercepts of the linear plots of $1/C_e$ versus $1/q_e$. The experimental data is well fitted by the Langmuir equation as shown by high correlation coefficients (R^2) in Table 3.2. The θ and b were also evaluated. The maximum adsorption capacities evaluated from Langmuir adsorption isotherms for CWS800 and CBS800 were 1.67 mol/kg and 1.68 mol/kg, respectively at pH 2.

The Langmuir constant, 'b', indicates the favorability of reaction. The dimensionless separation parameter R_L [= $\{1/(1 + bC_i)\}$] expresses the essential

characteristics of the Langmuir isotherm [18]. Here, C_i is the initial concentration of Cr (VI). The evaluated R_L values in all cases lie between 0 and 1, which indicate the favorable adsorption of Cr (VI) on the carbons.

Table 3.2. Estimated Langmuir isotherm parameters for Cr (VI) adsorption at 30°C.

Langmuir isotherm equation		Estimated isotherm parameters		
$1/q_e = 1/\theta \cdot b \cdot C_e + 1/\theta$		R^2	θ (mol/kg)	b (L/mol)
pH = 1	CWS800	0.99	1.50	8435
pH = 1	CBS800	0.99	1.51	8886
pH = 2	CWS800	0.95	1.67	1359
pH = 2	CBS800	0.96	1.68	1448

Since the chromium concentration was measured using ICP/AES spectrometer, the maximum total loading capacity is the actual amount of chromium removed by adsorption. It should be noted that Cr(III) ion generated after reduction of Cr(VI) do not adsorb on carbon surface at pH 1 and 2 as the adsorption of Cr(III) on CBS800 and CWS800 starts from pH 4 as shown in Fig. 3.7. Thus the maximum adsorption capacities mentioned above are due to adsorption of Cr(VI).

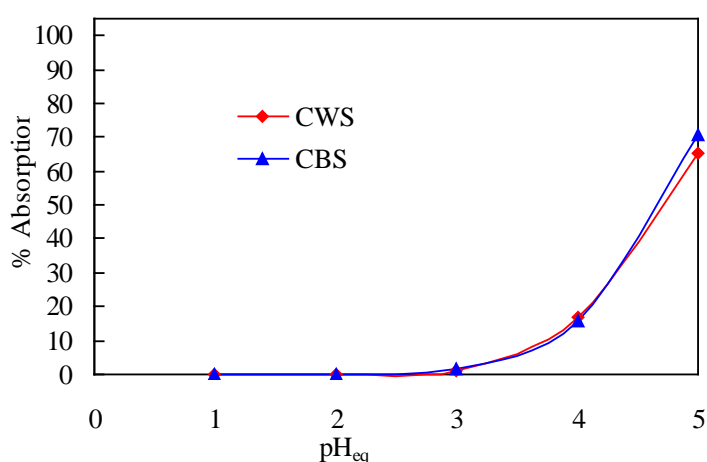


Fig. 3.7. Effect of pH on adsorption of Cr(III) on CBS800 and CWS800 from Cr(III) solution. Weight of adsorbent=25 mg; Volume of Cr(III) solution=15 ml; Chromium(III) concentration= 25 ppm; Shaking time= 24 h.

Chemical states of the adsorbed Cr on CBS800 and CWS800 at pH 2 were also examined by electron spin resonance measurement. Cr (III) containing unpaired electron is ESR positive and thus shows peak while Cr (VI) with no unpaired electron is ESR negative showing no peak[16]. Appearance of no peak (Figure is not shown) in chromium loaded CBS800 and CWS800 suggests that Cr adsorbed on CBS800 as well as CWS800 was in the form of Cr (VI).

3.3.3. Comparison of adsorption capacities with other adsorbents. Table 3.3. shows a comparison of the Cr(VI) adsorption capacity of CWS800 and CBS800 with other adsorbents as reported in the literature. Maximum adsorption capacities only among various carbons are compared in this table where the total chromium ion removed was evaluated. Since, in most of the literatures, maximum adsorption capacities was evaluated by measuring only Cr(VI) ion in the solution, the maximum adsorption capacity appears higher than the actual value. As Cr(VI) removal takes place by adsorption coupled reduction mechanism some amount of Cr(VI) get reduced to Cr(III) after adsorption which generally desorb back to solution. Thus to know the actual value of maximum adsorption capacity researcher, should measure the concentration of total chromium ions present in the solution as mentioned by Park *et al.* [14].

Table 3.3. Comparison of adsorption capacity, q, of various carbons for Cr (VI).

Carbon from	pH	Temp.	q (mol/kg)	Surface area	Reference
Groundnut husk	3	30 °C	0.22	-	[7]
<i>Casurina</i> <i>equisetifolia</i> leaves	3	30 °C	0.67	629 m ² /g	[19]
Coconut fiber	2	40 °C	0.42	343 m ² /g	[20]
Sugarcane bagasse	5	-	0.54	320 m ² /g	[21]
Eucalyptus saw dust	5	-	0.25	367 m ² /g	[21]
Barley straw	2	30 °C	1.68	792 m ² /g	This work
Wheat straw	2	30 °C	1.67	700 m ² /g	This work

It can be seen that the carbon produced from barley and wheat straws by a simple carbonization process are superior to many other activated carbons for chromium adsorption. The significantly high adsorption capacities of wheat and barley straw carbons compared with other adsorbents are attributable to their high surface areas. These carbonized materials show high adsorption capacities at acidic pH. Since most of the industrial effluents contaminated with Cr(VI) are highly acidic, these carbonized materials can be good alternatives for chromium removal.

3.4. Conclusions

High quality porous carbon can be prepared from waste straw by employing very simple method of carbonization. CBS800 and CWS800 are both primarily microporous. These carbons effectively remove Cr(VI) ion from solution, exhibiting high adsorption capacities, suggesting that waste straws can be employed as an alternative to conventional adsorbents for the adsorption of Cr(VI). The equilibrium was reached within 1 h of contact time. The high adsorption capacity and very fast kinetic of both type of carbons studied make them promising alternatives for Cr(VI) removal.

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Selective adsorption of precious metals from hydrochloric acid solutions using porous carbons prepared from barley straw and rice husk

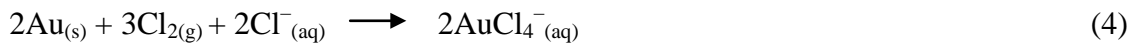
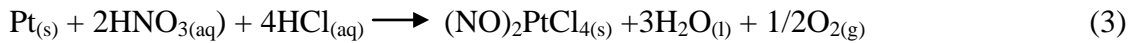
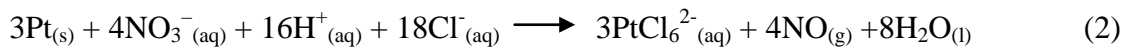
Porous carbon was prepared by carbonization from agro-waste such as rice husk and barley straw to evaluate the adsorption of precious and base metals from metal solutions. The effects of hydrochloric acid concentration, metal ion concentration, and contact time on adsorption were examined. Rice husk carbon was found to be highly selective for Au(III) and inert to Pt(IV), Pd(II) and other base metals. Barley straw carbon adsorbed these three precious metal ions, but was inert to base metal ions such as Cu(II), Fe(III) and Ni(II) *etc.* The maximum adsorption capacity of rice husk carbon for Au(III) was 0.76 mol/kg and the maximum adsorption capacity of barley straw carbon for Au(III), Pt(IV) and Pd(II) was 1.47, 0.39 and 0.64 mol/kg, respectively. The effectiveness of recovery of precious metals from industrial solution was also tested and barley straw carbon was found to be highly efficient and selective for the targeted metal ions in the presence of excess of other metal ions. Rice husk and barley straw carbons are thus potential alternatives to commercially available activated carbon as they have high selectivity and are efficient with low production costs.

4.1. Introduction

Precious metals are used extensively in jewelry, electronics, electroplating and medicine *etc.* [1]. Increasing demand and limited resources has encouraged precious

metals recovery from secondary metal-containing sources like electronic and industrial wastes. This recovery is also economically and environmentally beneficial [2]. Precious metals content in electronic waste was found to be higher than their content in ores [3]. Many studies are currently being undertaken to develop new or modified techniques for the separation and recovery of precious metals from electronic and industrial wastes [4-6].

The recovery of precious metals from secondary sources usually requires their separation from other metals. Classical lixiviation processes with aqua regia produce solutions containing chloro-complexes of precious metals and base metals [7]. This classical process suffers from various problems like emission of nitrogen oxides and formation of nitro and nitrosyl complexes of platinum group metals which are refractory compounds noted in Eqs. (1) – (4).



Modern lixiviation processes use hydrochloric acid containing chlorine gas instead of aqua regia. The chlorine gas oxidizes gold according to Eq. 4 in acidic solutions (based on the Eh-log[Cl⁻] diagram, Senanayake, 2004) [8]. The most important part of the hydrometallurgical precious metals recovery process is the selective separation of these metals. Adsorption is one of the most effective methods for preconcentration and separation of gold from aqueous solutions [9]. Selective adsorption of precious metals from acidic chloride solutions that also contain large quantities of other metals is difficult. The recovery of precious metals from hydrochloric acid by means of adsorption or solvent extraction is limited by elution or stripping (loaded sorbents stripping or solvent stripping) [10]. These loaded sorbents or solvents are often incinerated leaving ash containing precious metals. Since the

incineration of plastic ion exchange resins or commercially available activated carbon is energy intensive and costly, more effective sorbents with high selectivity, ease of incineration and cheap production are required.

Activated carbon has been the preferred adsorbent for many years in the gold recovery process due to its high adsorption capacity, high adsorption rate and good resistance to abrasion [11]. Increased use of activated carbon has necessitated the exploitation of abundant, readily available and low cost sources like agricultural by-products [12]. Activated carbon is a good adsorbent as it has an extended surface area, porous structure with micropores, mesopores and macropores, high adsorption capacity and a certain degree of surface reactivity due to the presence of appropriate functional groups. These properties are governed by both the nature of the raw materials and the processes used to obtain the activated carbon.

Rice husk and barley straw are currently not fully utilized and are discharged as waste, but can possibly be used as an alternative precursor for porous carbon. The aim of this study is to prepare low cost carbon from these wastes to replace expensive, commercially-available adsorbents for the recovery of precious metals.

4.2. Experimental

Carbons from rice husk and barley straw were prepared by carbonization process as discussed in section 2.2.1. of Chapter 2. The carbon prepared at 800°C carbonization temperature was used in this study. Metal adsorption on porous carbon is influenced by their surface characteristics, and these physical and chemical properties are refer to Table 4.1. The specific surface area was measured using a Belsorp 18 PLUS-SP (BEL. JAPAN. INC). The pH value required to give zero net surface charge, designated the point of zero charge (PZC), was measured by means of a mass titration method [12]. The specific surface area of barley straw carbon was much higher than that of rice husk carbon. The PZC value suggests that both rice husk and barley straw carbons have positively charged surfaces at acidic pH.

Table 4.1. Characteristics of rice husk and barley straw carbons.

Sample	Specific surface area	Average pore diameter	PZC
Rice husk carbon	319 m ² /g	2.42 nm	8.54
Barley straw carbon	792 m ² /g	2.52 nm	9.2

Batchwise adsorption behavior tests of porous carbon for metal ions at different concentrations of hydrochloric acid were carried out. Individual metal solutions (0.2 mM) were prepared using various concentrations of hydrochloric acid. To obtain equilibrium 15 ml of the metal solution was mixed with 25 mg adsorbent and shaken for 24 h at 30°C.

The adsorption isotherm experiment was conducted by mixing 15 ml test solution containing 0.2 - 5 mM individual metal ions with 25 mg adsorbent, then shaking for 24 h at 30 °C. Adsorption kinetics experiments were conducted by shaking 15 ml of 1 mM Au(III) solution with 25 mg adsorbent for 5 min – 24 h at 30°C.

The effect of adsorbent dose on adsorption of precious metal ion from industrial solution was studied by adding 15 ml industrial solution containing 7,270 mg/L Cu(II), 4,744 mg/L Ni(II), 18,652 mg/L Fe(III), 5 mg/L Pd(II) and 134 mg/L Au(III). The adsorbent dose was varied from 5 to 50 mg and the mixture was shaken for 24 h at 30°C.

The concentrations of metal ions before and after adsorption were measured by a Shimadzu model ICPS-8100 ICP/AES spectrometer. The % adsorption and metal uptake capacity, q, for each metal ion was calculated as follows:

$$\% \text{ Adsorption} = [(C_i - C_e)/C_i] \times 100 \quad (5)$$

$$q = [(C_i - C_e)/W] \times V \quad (6)$$

where, C_i, C_e, W and V are the initial and equilibrium metal concentrations, dry weight of adsorbent and solution volume, respectively.

Thermogravimetric analysis was performed on the carbon materials before and after adsorption of gold using a Seiko Instruments model TG/DTA 6300 thermogravimeter. About 5 mg of each sample was heated from 10 to 800°C at a heating rate of 10 °C/min.

4.3. Results and discussion

Figure 4.1. (a) shows the % adsorption of Au(III), Pt(IV), Pd(II), Cu(II), Fe(III), Ni(II) on rice husk carbon at varying concentrations of hydrochloric acid. Au(III), Pd(II), and Pt(IV) form anionic chloride complex of the form AuCl_4^- , PdCl_4^{2-} , and PtCl_6^{2-} respectively in strong hydrochloric acid concentration [8, 14]. Metal ions like Cu(II), Fe(III) and Ni(II) exist mostly as cationic or neutral species and the concentration of anionic chlorides is significant only at higher chloride concentration [15]. The rice husk was found to be highly selective for Au(III) and exhibited negligible affinity for other metal ions. The change in % adsorption of Au(III) was insignificant over the whole hydrochloric acid concentration range from 0.1 to 6.0 M. This adsorption behavior indicates that carbonized rice husk is suitable for separation of gold from other base metal ions in acidic solutions. The high affinity of rice husk carbon for Au(III) is due to the greater potential of AuCl_4^- to reduce than PtCl_4^{2-} and PdCl_4^{2-} , as it has a higher standard reduction potential [3], for example for gold, $E^\circ (\text{AuCl}_4^-/\text{Au}) = 1.00 \text{ V}$, for platinum, $E^\circ (\text{PtCl}_4^{2-}/\text{Pt}) = 0.73 \text{ V}$ and for palladium, $E^\circ (\text{PdCl}_4^{2-}/\text{Pd}) = 0.62 \text{ V}$ [16].

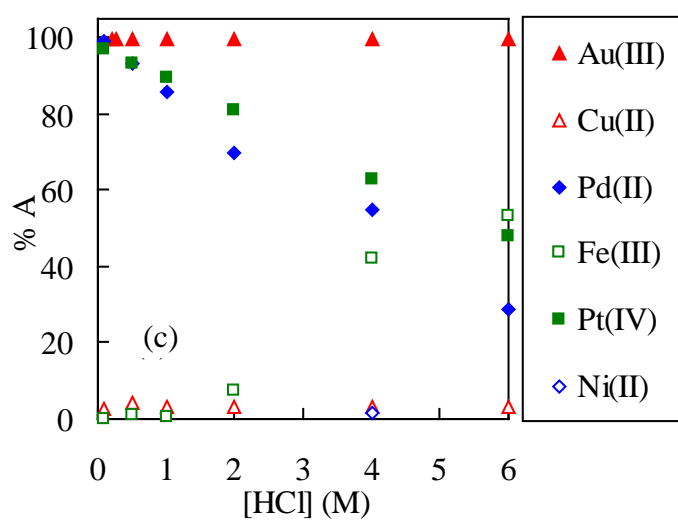
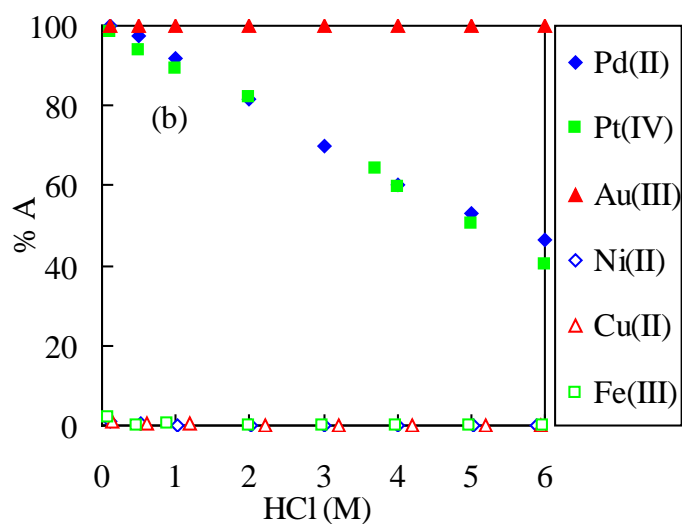
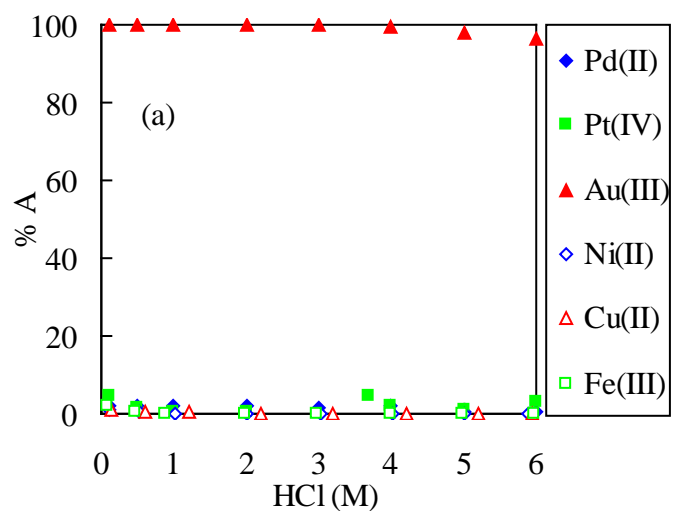


Fig. 4.1. Adsorption of different metal ions as a function of hydrochloric acid concentration on (a) rice husk carbon, (b) barley straw carbon and (c) commercial

activated carbon. Initial concentration of metal ions = 0.2 mM, wt. of carbon = 25 mg, vol. of solution = 15 ml, shaking time 24 h, temperature = 30°C.

Figure 4.1 (b) shows the % adsorption of Au(III), Pt(IV), Pd(II) and other base metal ions on barley straw carbon at varying hydrochloric acid concentrations. Unlike rice husk carbon, barley straw carbon adsorbs all three precious metal ions completely at 0.1 M hydrochloric acid concentration. By increasing the hydrochloric acid concentration from 0.1 to 6.0 M, the adsorption of Pt(IV) and Pd(II) slowly decreases, but the adsorption of Au(III) remains almost unaffected.

The high selectivity of barley straw and rice husk carbons to precious metal ions over other base metal ions in acidic solution is due to its positively charged surface as it adsorbs negatively charged species by electrostatic attraction. Since other base metal ions coexist in solution, partly in the form of cationic species, they cannot adsorb onto the carbon surface because of their similar electronic charges.

Adsorption tests were also carried out on commercially available activated carbon for comparison. Figure 4.1. (c) shows the % adsorption of Au(III), Pd(II), Pt(IV), Cu(II), Fe(III) and Ni(II) at varying hydrochloric acid concentrations. Unlike rice husk and barley straw carbons, the commercially available activated carbon exhibited considerable adsorption for all metals tested except for Cu(II). The adsorption of Fe(III) greatly increased with increasing hydrochloric acid concentrations of higher than 2 M.

Adsorption isotherm tests were carried out on rice husk carbon for Au(III) with 1 M hydrochloric acid as the rice husk carbon selectively adsorbs Au(III) (Fig. 4.2). Adsorption isotherm tests were also carried out on all three precious metals on barley straw carbon at a constant hydrochloric acid concentration of 1 M (Fig. 4.2). For both types of carbon metal ion adsorption increased with increasing metal ion equilibrium concentrations in low concentration regions and plateaus were observed at high concentration regions exhibiting a Langmuir type adsorption. Maximum metal uptake capacities were evaluated from values in the plateau regions which were 0.78 mol/kg for Au(III) on rice husk carbon and 1.49, 0.62 and 0.39 mol/kg for Au(III), Pd(II) and

Pt(IV), respectively, on barley straw carbon.

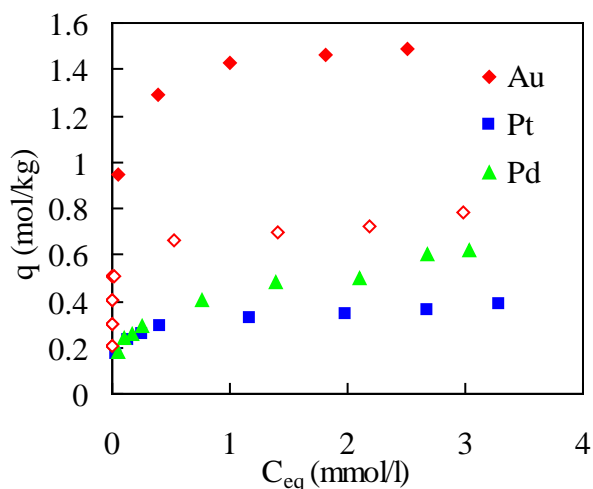


Fig. 4.2. The adsorption isotherms of Au(III), Pt(IV) and Pd(II) ions on carbons (open symbol for rice husk carbon and closed symbol for barley straw carbon). C_{eq} = Equilibrium concentration, q = amount of metal uptake, $[HCl] = 1$ M, wt. of carbon = 25 mg, vol. of solution = 15 ml, shaking time = 24 h, temperature = 30°C.

Consequently, the adsorption isotherm data was fitted with the following Langmuir equation.

$$C_e/q_e = (1/q_m)C_e + (1/Kq_m) \quad (7)$$

where:

q_e = amount adsorbed at equilibrium (mol/kg)

C_e = equilibrium Cr concentration in solution (mol/L)

q_m and K are Langmuir isotherm constants, which are related to maximum adsorption capacity and equilibrium constant, respectively, were determined from the slope and intercepts of the linear plots of C_e/q_e versus C_e and listed in Table 4.2. The experimental data is well fitted by the Langmuir equation as shown by high correlation coefficients (R^2) in Table 4.2.

Table 4.2. – Estimated Langmuir isotherm parameters at 30°C.

Langmuir isotherm equation $C_e/q_e = (1/q_m)C_e + (1/Kq_m)$		Estimated isotherm parameters		
		R^2	q_m (mol/kg)	K (L/mol)
Rice husk carbon	Au(III)	0.99	0.76	32915
Barley straw carbon	Au(III) Pd(II) Pt(IV)	0.99 0.98 0.99	1.47 0.64 0.39	68180 3929 8615

These results show that rice husk carbon is highly selective for Au(III) ion with an adsorption capacity of 0.78 mol/kg whereas barley straw carbon adsorbs Au(III), Pt(IV) as well as Pd(II) with much higher adsorption capacities than rice husk carbon. The higher adsorption capacities of barley straw carbon compared with rice husk carbon is attributed to its high specific surface area as listed in Table 4.1. For both types of adsorbents the observed high adsorption capacity for Au(III) is due to reduction of adsorbed Au(III) to its elemental form as shown in reaction (8), which creates active site vacancies for further adsorption, leading to an apparent uptake of higher amounts of gold.



Figure 4.3 shows scanning electron micrograph images of carbon taken after the adsorption of Au(III). In these images, white particles of elemental gold are present. The formation of elemental gold during adsorption was further confirmed by an X-ray diffractogram of carbon taken after the adsorption of gold (Fig. 4.4.). Sharp peaks at 2θ values of 38, 44, 64 and 77 degrees corresponding to elemental gold were observed.

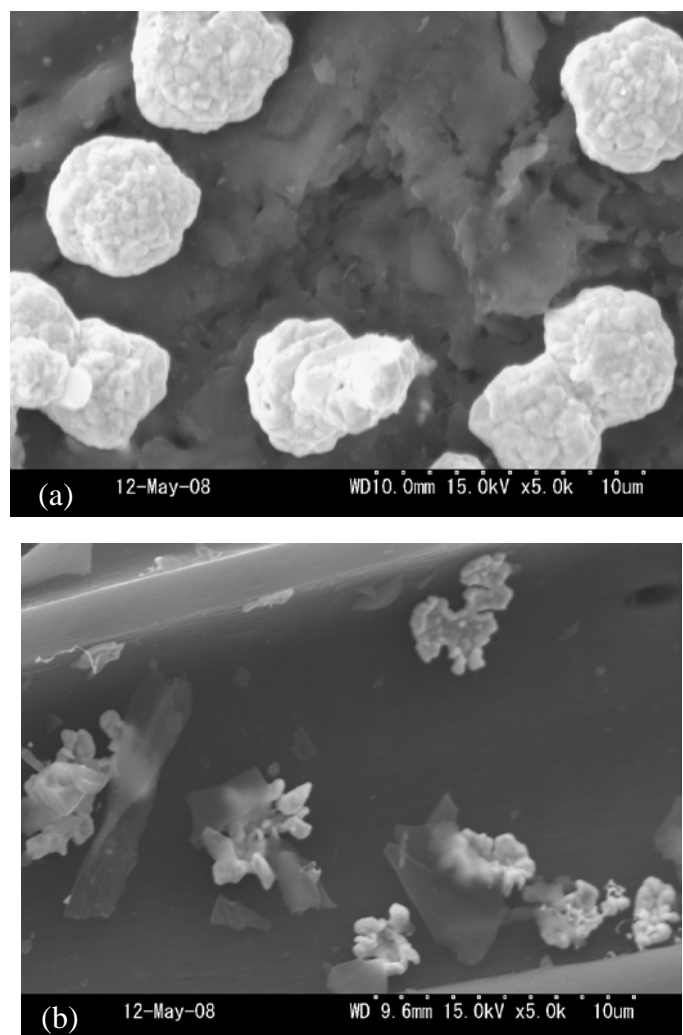


Fig. 4.3. SEM images of (a) rice husk carbon and (b) barley straw carbon after the adsorption of Au(III).

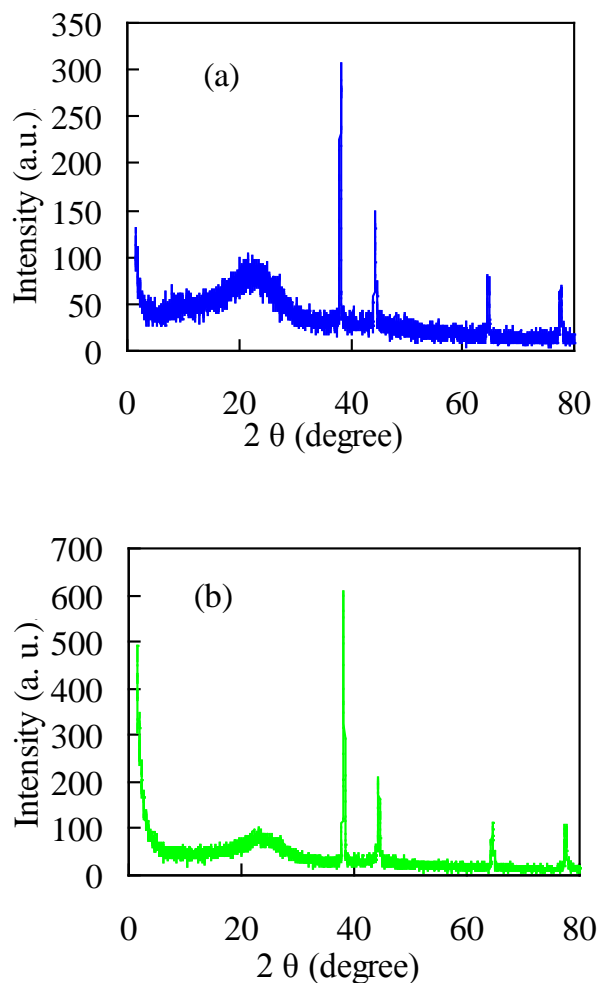


Fig.4.4. X-ray diffraction pattern of Au(III) loaded (a) rice husk carbon and (b) barley straw carbon.

The adsorption kinetics of Au(III) on porous carbon was studied using a 1 mM Au(III) solution in 1 M HCl as shown in Fig.4.5. The adsorption rate of Au(III) on porous barley straw carbon is so fast that equilibrium was reached within 1 h of contact time. The rate of adsorption on porous rice husk carbon is slower than that of barley straw carbon, and it takes 12 h to reach equilibrium. Barley straw carbon is thus the preferred adsorbent because it has a faster uptake rate, higher adsorption capacity and high selectivity for all precious metals. Even though its rate of adsorption is slightly lower, the main advantage of rice husk carbon is high selectivity for gold over other precious metals and base metals.

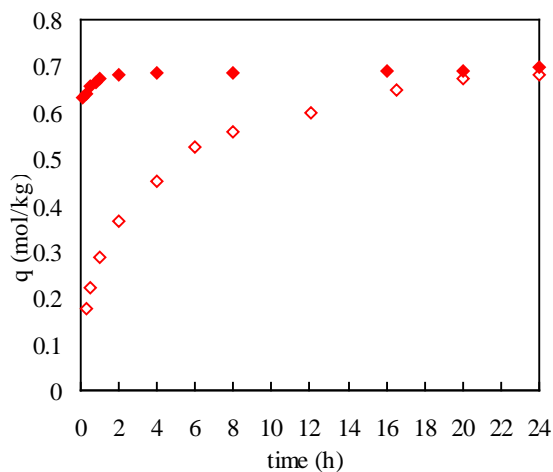


Fig. 4.5. Effect of contact time on the adsorption of Au(III) onto carbon (open symbol for rice husk carbon and closed symbol for barley straw carbon). Initial concentration of Au(III) = 1 mM, [HCl] = 1 M, wt. of carbon = 25 mg, vol. of solution = 15 ml, temperature = 30°C.

Figure 4.6 shows the effect of adsorbent dose on adsorption of precious metal from industrial solution. It can be seen that the rice husk carbon selectively adsorbs Au(III) ion and shows negligible adsorption for other metal ions that coexist in the industrial solution. Whereas barley straw carbon adsorbs Au(III) as well as some amount of Pd(II) but do not adsorb other base metal ions. The percentage adsorption of Au(III) increases with increasing the solid liquid ratio upto 2 g/L in both types of carbon. 27% of Au(III) was adsorbed by rice husk carbon at 2 g/L. Barley straw carbon removes almost 100% of Au(III) and adsorbs 16% of Pd(II) at 2 g/L.

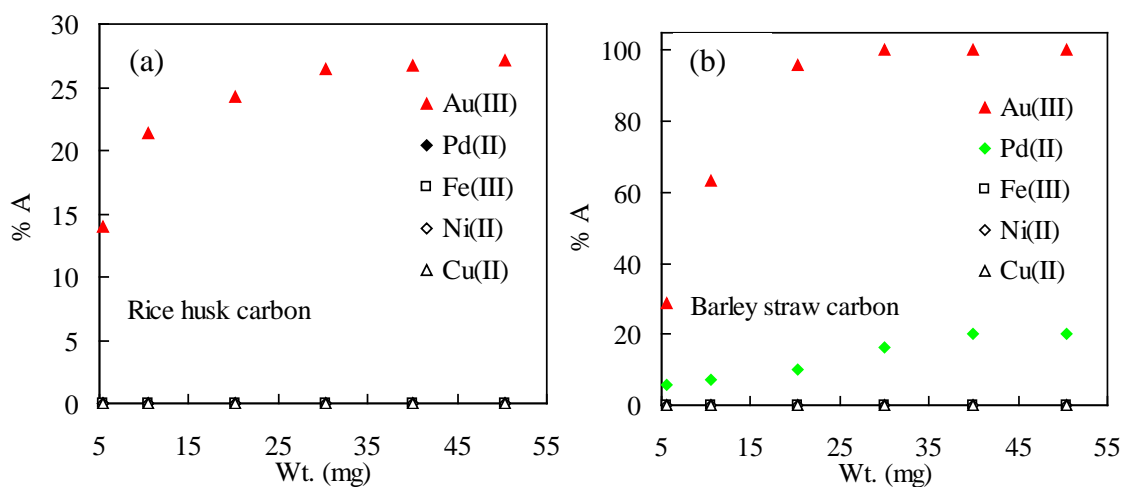


Fig. 4.6. Effect of adsorbent dose on adsorption of different metal ions from industrial

solution. $[HCl] = 1.5 \text{ M}$, vol. of solution = 15 ml, shaking time = 24 h, temperature = 30°C .

As mentioned earlier, adsorbed precious metals can be easily recovered by simply burning the metal-loaded carbon materials. Figure 4.7. shows the thermogravimetric plot of original carbon and gold loaded gel, and shows that all carbon was completely burnt off below 600°C . The recovery of adsorbed gold from carbon can thus be carried out by burning the gold-loaded carbon at 600°C in air as shown by the thermogravimetric plot. The carbon is converted into carbon monoxide and carbon dioxide, leaving some residue. The residue left after burning was analyzed for its chemical constituents using a HITACHI S3000 EDAX (Energy Dispersive X-ray Spectrometry). The EDAX result showed that metallic gold as well as silica was left after burning the gold adsorbed carbon. The silica may be removed by washing the residue with 2 M NaOH at 80°C for 2 h as silica is taken up by the filtrate while gold remains on the filter paper as residue.

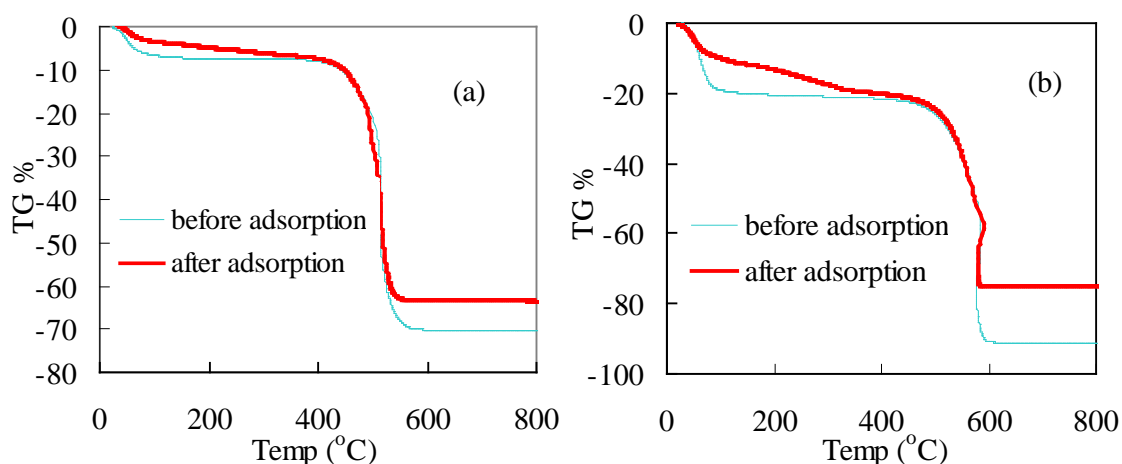


Fig. 4.7. Thermogravimetric plot of (a) rice husk carbon and (b) barley straw carbon before and after the adsorption of gold.

4.4. Conclusions

This study shows that rice husk carbon is highly selective for Au(III), and that barley straw carbon is highly selective for Au(III) and other precious metals over various base metals. The adsorption of Au(III) on both adsorbents is nearly independent

of hydrochloric acid concentration, which is advantageous in practical applications. The very fast metal ion adsorption rate of barley straw carbon is an additional advantage. The enhanced adsorption capacity as a result of Au(III) to Au(0) reduction, high selectivity and very fast adsorption rate for carbons generated from discarded agro-waste can make rice husk carbon and barley straw carbon a promising alternative adsorbent for precious metals and Au(III) recovery from industrial waste using chloride solution.

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Recovery of precious metal using wheat straw carbon

Wheat straw, an agrowaste was carbonized using simple single step carbonization process to obtain a porous carbon, which was investigated for adsorption of precious and base metals from metal solutions under acidic conditions. The effects of hydrochloric acid concentration, metal ion concentration, and contact time on adsorption were examined in batch mode. Wheat straw carbon exhibited selectivity only for precious metal ions tested, but was inert to base metal ions such as Cu(II), Fe(III) and Ni(II). The maximum adsorption capacity of carbonized wheat straw from batch adsorption test for Au(III), Pt(IV) and Pd(II) was 1.15, 0.19 and 0.4 mol/kg, respectively. Column test for metal solution containing Au(III), Pt(IV), Pd (II) and Cu(II) in mutual system revealed higher selectivity and efficiency for precious metals. The adsorption capacity of Au(III) in column experiment was also found to be 1.01 mol/kg. The high adsorption capacity of Au(III) in column test was attributed to its fast kinetics. Carbonized wheat straw is thus potential alternative to commercially available activated carbon as it has high selectivity and is efficient with low production costs.

5.1. Introduction

Limited resources and increasing demand of precious metals like gold, palladium and platinum has encouraged precious metals recovery from secondary metal-containing sources like electronic and industrial wastes [1]. Recycling and reuse of metals is very important since it expands the supply of feedstocks for advanced materials and prevents the practice of excessive mining. This recovery is also economically and environmentally beneficial [2]. Many studies are currently being undertaken to develop new or modified techniques for the separation and recovery of precious metals from electronic waste [3-5].

The usual practice for the recovery of the metal from such wastes includes dismantling the devices and treating each part separately for metal recovery. The part

such as printed circuit boards (PCBs) are leached with hydrochloric acid containing chlorine gas under modern lixivation processes [6]. The chlorine gas is converted into hypochlorous acid which is an oxidant that dissolves metallic elements and the hypochlorous acid is finally converted into hydrochloric acid. The most important part of the hydrometallurgical precious metals recovery process is the selective separation of these metals. Adsorption is one of the most effective methods for preconcentration and separation of gold from aqueous solutions [7] however, selective adsorption of precious metals from acidic chloride solutions that also contain large quantities of other metals is difficult [8].

Activated carbon has been the preferred adsorbent for many years in the gold recovery process due to its high adsorption capacity, high adsorption rate and good resistance to abrasion [9]. Increased use of activated carbon has necessitated the exploitation of abundant, readily available and low cost starting materials like agricultural by-products for its preparation [10]. Biomass, such as agricultural products does not emit extra carbon dioxide when burned therefore expected to be carbon-neutral and petrochemical-independent [11]. Carbonization of carbon containing raw materials is the prerequisite step for preparation of carbon but the porosities of carbon is not sufficiently developed to match the need for practical uses. Thus generally carbonization is simultaneously followed by thermal activation (carbonization under flow of CO₂ or steam) or chemical activation (carbonization after chemical treatment with reagent like ZnCl₂, H₃PO₄ or KOH) or combination of both [12]. Consequently, the preparation procedure of highly porous carbon becomes difficult and expensive.

In the present work, porous carbon material was prepared from low-cost agrowaste, wheat straw by applying very simple method of carbonization without using any activation process. Thus prepared carbon has been tried as adsorbents for the recovery of precious metal from aqueous solutions.

5.2. Experimental

5.2.1 Preparation of carbonized materials. Carbon from wheat straw was prepared by

carbonization process as discussed in section 2.2.1. of Chapter 2. The carbon prepared at 800°C carbonization temperature was used in this study.

5.2.2. Preparation of synthetic test solutions. Sample solutions of various metal ions for the adsorption test were prepared by using commercially available analytical grade salts without further purification. For the preparation of Cu(II), Fe(III), Ni(II), Pd(II) test solution, respective chloride salts were used. And for the preparation of Au(III), and Pt(IV) solutions, $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, respectively were used. Test solutions of various individual metal ions for the adsorption test were prepared in varying concentrations of hydrochloric acid.

5.2.3. Adsorption tests. The adsorption tests were carried out in batch mode by adding 25 mg of adsorbent to 15 ml of a metal solution in a 50 ml conical flask. The mixture was shaken in a thermostated shaker at 30°C and 150 rpm. The shaking time was 24 h for all experiments except for the kinetic experiments. After 24 h, the suspended mixture was filtered through a filter paper. The filtrate was analyzed for its metal content using Shimadzu model ICPS-8100 ICP/AES spectrometer. All the experiments were conducted in duplicate and mean values are reported in this paper. The maximum deviation observed was less than 5%.

5.2.4. Column test. The column test for the separation of low concentrations of Au(III), Pd(II), and Pt(IV) from a high concentration of Cu(II) was conducted. A 100 mg of wheat straw carbon was soaked in distilled water for 1 h. Then the adsorbent was filled into a column with inner diameter of 8 mm. The height of the bed was 10 mm. Prior to passing the test solution, the column was conditioned with distilled water followed by 1 M hydrochloric acid solution for 24 h. The synthetic solution containing 0.1 mmol/L Au(III), 0.1 mmol/L Pd(II), 0.1 mmol/L Pt(IV) and 3.2 mmol/L Cu(II) in 1 M HCl was pumped into the column with a constant volume speed of 5 ml/h using an Iwaki model PST-100N peristaltic pump. Effluent was collected by Bio-Rad model 2110 fraction collector and the concentration of metals was analyzed.

5.3. Results and discussion

5.3.1. Effect of hydrochloric acid concentration on the adsorption of some metal ions. The adsorption behavior of the wheat straw carbon for Au(III), Pt(IV), Pd(II), Cu(II), Fe(III) and Ni (II) with initial concentration 0.2 mM for each metal ion and at varying hydrochloric acid concentrations (0.1 to 6 M) is shown in Fig. 5.1. (a). From the figure it is clear that wheat straw carbon quantitatively adsorb Au(III), Pt(IV) and Pd(II) at hydrochloric acid concentration 0.1 to 1 M, whereas showed negligible affinity for other base metals tested. By increasing the hydrochloric acid concentration from 0.1 up to 6 M, the adsorption of Pt(IV) and Pd(II) slowly decreases but the adsorption of Au(III) remains almost unaffected. This result indicates that the precious metals can be selectively recovered from any other coexisting base metal ions in hydrochloric acid medium using this porous carbon.

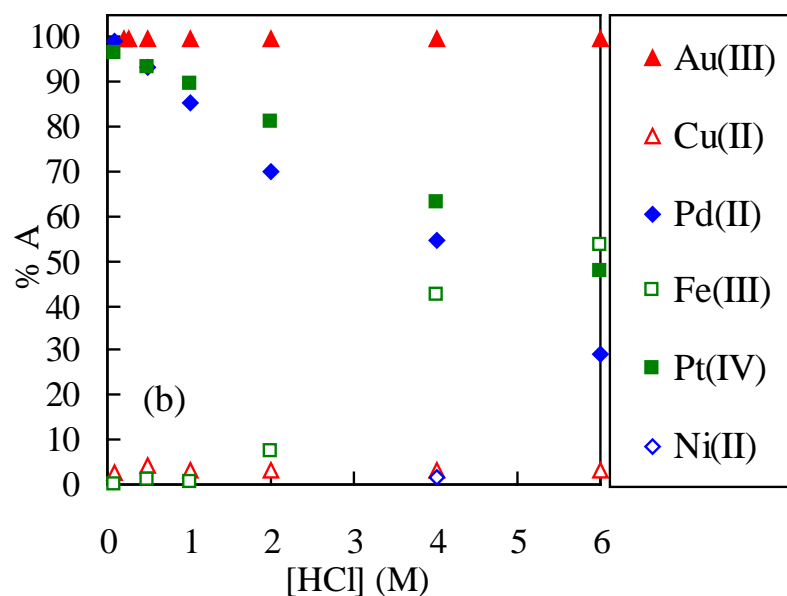
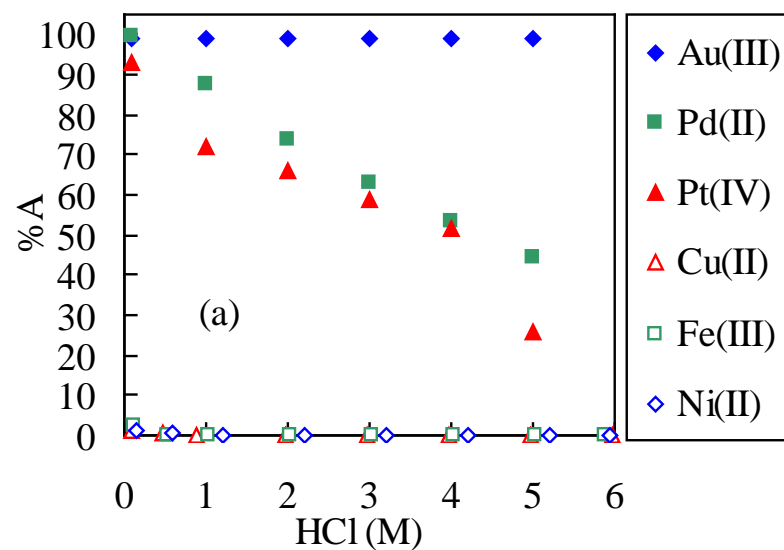


Fig. 5.1. Adsorption of different metal ions as a function of hydrochloric acid concentration on (a) wheat straw carbon, and (b) commercial activated carbon. Initial concentration of metal ions = 0.2 mM, wt. of adsorbent = 25 mg, vol. of solution = 15 ml, shaking time = 24 h, temperature = 30°C.

Adsorption tests were also carried out on commercially available activated carbon for comparison. Fig. 5.1. (b) shows the % adsorption of Au(III), Pd(II), Pt(IV), Cu(II), Fe(III) and Ni(II) at varying hydrochloric acid concentrations. Unlike wheat straw carbon, the commercially available activated carbon exhibited considerable

adsorption for all metals tested except for Cu(II). The adsorption of Fe(III) greatly increased with increasing hydrochloric acid concentrations of higher than 2 M.

5.3.2. Adsorption isotherms. Adsorption isotherm tests for Au(III), Pt(IV) and Pd(II) onto wheat straw carbon were carried out at a constant hydrochloric acid concentration of 1 M (Fig. 5.2.). The metal ion adsorption increased with increasing metal ion equilibrium concentrations in low concentration regions and plateaus were observed at high concentration regions exhibiting a Langmuir type adsorption. Maximum metal uptake capacities were evaluated from values in the plateau regions which were 1.15, 0.19, and 0.4 mol/kg for Au(III), Pd(II) and Pt(IV), respectively.

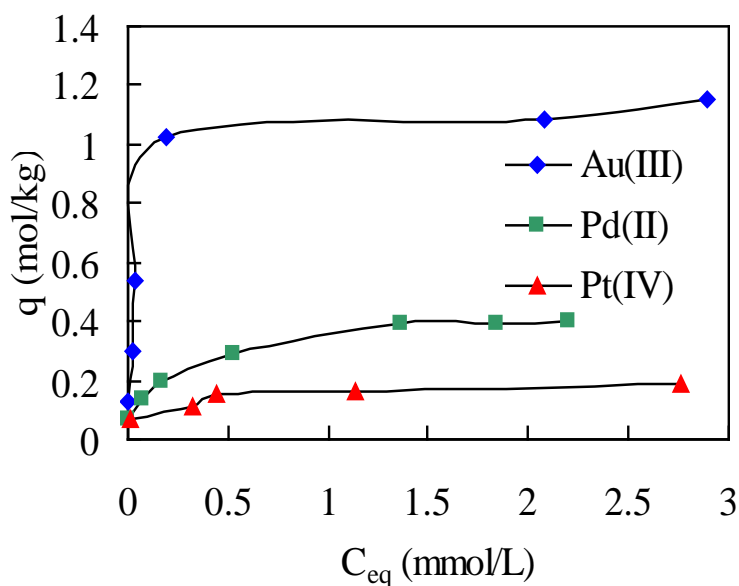


Fig. 5.2. The adsorption isotherms for Au(III), Pt(IV) and Pd(II) on wheat straw carbons. [HCl] = 1 M, vol. of solution = 15 ml, wt. of adsorbent = 25 mg, shaking time = 24 h, temperature = 30°C.

The observed high adsorption capacity for Au(III) is due to reduction of adsorbed Au(III) to its elemental form, which creates active site vacancies for further adsorption, leading to an apparent uptake of higher amounts of gold. Fig. 5.3 shows scanning electron micrograph images of carbon taken after the adsorption of Au(III). In these images, white particles of elemental gold are present. The formation of elemental gold during adsorption was further confirmed by an X-ray diffractogram of carbon taken

after the adsorption of gold (Fig. 5.4.). Sharp peaks at 2θ values of 38, 44, 64 and 77 degrees corresponding to elemental gold were observed.

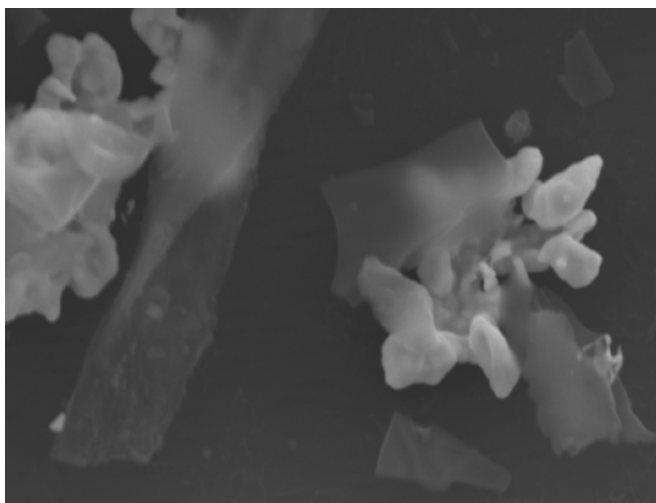


Fig. 5.3. SEM image of wheat straw carbon after the adsorption of Au(III).

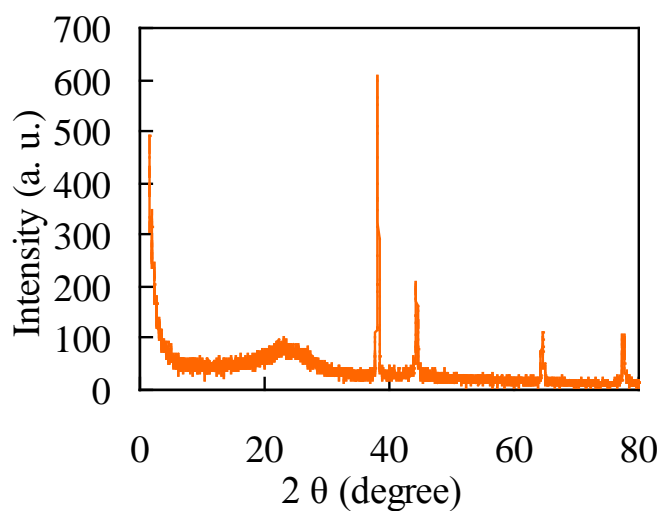


Fig. 5.4. X-ray diffraction pattern of Au(III) loaded wheat straw carbon.

5.3.3. Column test. Based on the batchwise adsorption tests of various metal ions on the wheat straw carbon (Fig. 5.1.(a) and Fig. 5.2.), wheat straw carbon was found to be good adsorbent for gold, palladium, and platinum with a higher selectivity and capacity. Thus, a mutual chromatographic separation test was carried out to separate low concentration of these precious metals from a mixture containing excess of Cu(II), a representative base metal coexisting in practical waste solutions using a column packed

with the wheat straw carbon. In the breakthrough curve as shown in Fig. 5.5., it is clearly seen that the breakthrough of Cu(II) occurred immediately after the start of the operation, but breakthrough of Pd(II) and Pt(IV) was observed after 22 and 20 h, respectively. The breakthrough of Au(III) occurred after 182 h. More than 1200 ml of solution were passed through the column for complete saturation of the carbon. The gel was completely saturated by Pd(II) in 90 h, by Pt(VI) in 80 h and by Au(III) in 252 h. The adsorption capacity of the gel evaluated from the column adsorption test was 0.100, 0.102, and 1.015 mol/kg for Pd(II), Pt(VI) and Au(III), respectively. The adsorption capacity of Pt(VI) and Pd(II) in this case are much lower than those observed in batch tests. But the adsorption capacity of Au(III) is almost equals to that in batch test (1.15 mol/kg). In case of most of the adsorbent the adsorption capacity in column test is much lower than the values observed in the batchwise adsorption isotherm study, which is attributed to the continuous flow of the solution, competitive adsorption, lower metal concentration compared to that in the isotherm test, and slower reduction kinetics in the case of gold [6, 13].

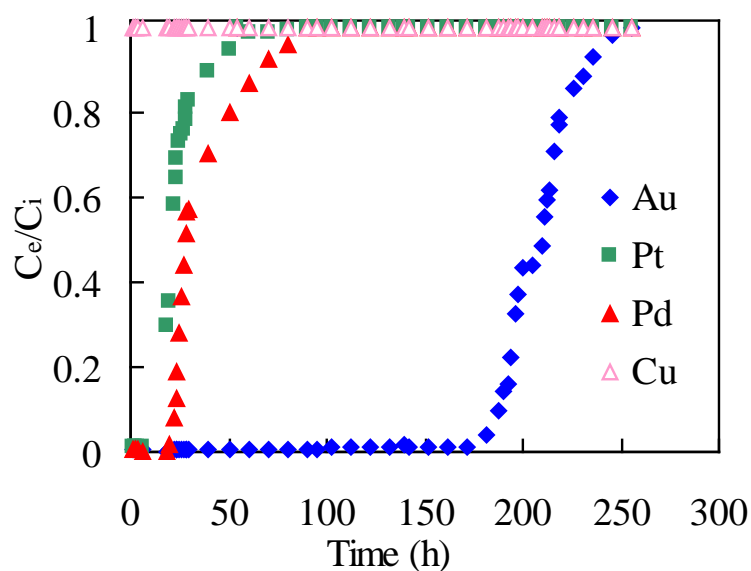


Fig. 5.5. Breakthrough profiles for Cu(II), Au(III), Pd(II) and Pt(IV). Feed concentration: Cu(II) = 3.2 mmol/L, Au(III), Pd(II), Pt(IV) ~ 0.1 mmol/L, flow rate = 5 ml/h.

The high adsorption capacity of Au(III) in column study in this case is attributed to fast kinetics of Au(III) adsorption on wheat straw carbon as shown in Fig. 5.6. Fig. 5.6. shows that the adsorption rate of Au(III) on porous wheat straw carbon is so fast that equilibrium was reached within 15 min of contact time using 0.1 mM Au(III) solution in 1 M HCl. The adsorption capacity of Pt(VI) and Pd(II) in column test are much lower than those observed in batch adsorption isotherm study eventhough their kinetics are fast as well as seen in Fig. 5.6., which is possibly attributable to competitive adsorption and lower metal concentration compared to that in the isotherm test.

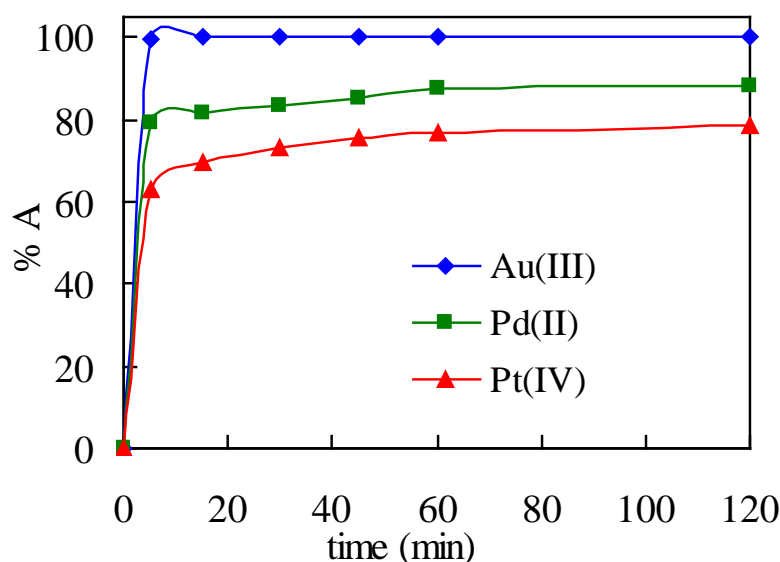


Fig. 5.6. Effect of contact time on the adsorption of Au(III), Pd(II) and Pt(IV) onto wheat straw carbon. Initial concentration of metal ions = 0.1 mM, [HCl] = 1 M, vol. of solution = 15 ml, wt. of adsorbent = 25 mg, temperature = 30°C.

The capacities for precious metals in column test are comparatively high compared with those for other adsorbents, as shown in Table 5.1. [6, 13]. These results suggest that effective mutual separation and preconcentration of precious metals especially Au(III) away from base metals using wheat straw carbon can be satisfactorily achieved also in continuous flow system which is generally used for practical waste solutions.

Table 5.1. Comparison of Adsorption Capacities of Wheat Straw Carbon for Au(III), Pd(II) and Pt(IV) with Other Adsorbents in Column mode.

adsorbent		[H ⁺]	flow rate	adsorption capacity (mol/kg)			Ref
name	dry weight			Au(III)	Pd(II)	Pt(IV)	
phosphine sulphide type macroporous polymer A	1.6 g	1 M	17.7 ml/min	0.162	0.022		[13]
phosphine sulphide type macroporous polymer B	1.6g	1 M	17.7 ml/min	0.159	0.071		[13]
modified waste paper	0.1 g	1 M	6 ml/h	0.26	0.60	0.31	[6]
wheat straw carbon	0.1 g	1 M	5 ml/h	1.01	0.10	0.10	this work

5.3.4. Thermogravimetric analysis. It has been tried to elute the adsorbed precious metals using 0.1 M thiourea in 1 M hydrochloric acid which has been proved to be the best elutant for precious metal ions [13, 14]. The percentage recovery for all the three precious metal ions was less than 1%. It is very difficult to elute the adsorbed precious metals from carbon and the easy way to recover the adsorbed precious metals is to burn the metal-loaded carbon materials. Fig. 5.7. shows the thermogravimetric plot of original carbon and gold loaded gel, and shows that the carbon was completely burnt off below 600°C. The recovery of adsorbed gold from carbon can thus be carried out by burning the gold-loaded carbon at 600°C in air as shown by the thermogravimetric plot.

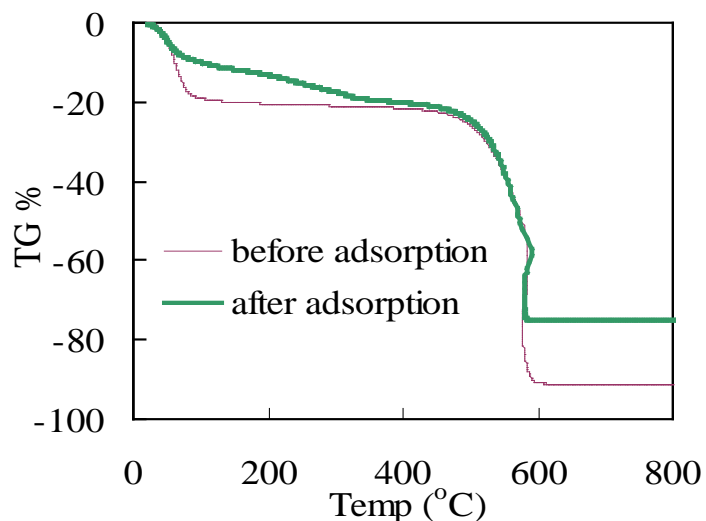


Fig. 5.7. Thermogravimetric plot of wheat straw carbon before and after the adsorption of gold.

5.4. Conclusions

The study indicated wheat straw carbon exhibited excellent adsorption capacity, high selectivity and fast kinetic for precious metals tested, especially Au(III) in hydrochloric acid media using batch as well as a column system. With high efficiency, the method of its preparation is simple and cheaper. The wheat straw carbon generated from discarded agrowaste thus can be a promising alternative adsorbent in industrial applications for preconcentration and separation of precious metals.

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Chemical modification of carbonized wheat and barley straw using HNO₃ and the adsorption of Cr(III)

The effects of oxidation using HNO₃ on the properties of the carbonized wheat and barley straw were investigated by measuring different properties such as specific surface area, PZC, total surface acidic groups as well as FTIR and TG-DTA analysis. A small decrease in the specific surface area due to pore blockage was observed after oxidation. After oxidation, the acidity was increased considerably and the point of zero charge shifted from approximately pH 9 to 2 in both types of carbons. By the oxidation of the carbon with nitric acid, carboxylic groups were produced as shown by absorption peaks at 1750 cm⁻¹ in the FTIR spectra. Boehm titration results showed that the number of carboxyl groups increased by approximately 11 fold after oxidation. The oxidized carbon samples were compared with the unoxidized original carbon samples for Cr(III) adsorption. It was observed that the oxidized carbons exhibit high adsorption efficiencies for Cr(III) ions compared to the original carbonized straws and this can be correlated to the decrease in PZC which is mainly due to the increase in carboxylic functional groups in the oxidized carbonized straws and these are responsible for their cation ion exchange phenomenon.

6.1. Introduction

Activated carbons are versatile adsorbents due to their extended surface area, high adsorption capacity, microporous structure and special surface reactivity [1]. The most important application of activated carbon is its use in separation and purification technologies. The consumption of activated carbon is ever increasing due to increasing

industrialization and pollution. Lignite coal, peat, wood and coconut shell have been used to prepare activated carbons [2]. Since such carbon sources are either limited or very expensive, production of carbon materials from agricultural wastes is required. Their advantages as carbon feedstocks include abundant availability and renewability, low cost and good quality carbon generation. It is a well established fact that the sorption properties of carbon materials are essentially influenced by their surface characteristics *i.e.* physical and chemical surface properties.

Although the adsorptive properties of carbons are controlled by their physical or porous structure [3], but they are strongly influenced by the chemical nature of the surface [4-6]. Surface functional groups like carboxyls, phenols, lactones, aldehydes, ketones, quinones, hydroquinones, have been postulated to exist on carbon surfaces [7]. Due to these functional groups the carbon will have an acidic or a basic character. The presence of various functional groups on the carbon surface depends on the nature of the activation process and the surface post-treatments [8,9].

The ion exchange capacity of carbons depends on surface functionality [10]. The surface charge of a carbon in aqueous suspension is also conditioned by its surface functional groups. These two properties affect the adsorption capacity. The oxidation of carbon leads to the formation of various surface acidic functional groups and also decreases the PZC of carbon, which enhances the adsorption of cationic metal ions from solution [11].

Surface modification of carbons can be achieved by various physiochemical methods. The chemical oxidation of carbon materials is a frequently used method to introduce surface oxygen groups as ion exchanging sites. Various oxidative reagents like nitric acid, sulfuric acid, hydrogen peroxide, ammonium persulphate, and fluorine gas are used for this purpose [12-15]. Several types of surface functional groups can be produced by oxidation treatments. Carboxylic, phenolic, lactones and peroxides have been suggested as acidic surface groups produced by oxidation treatments. Among the oxidation treatments, nitric acid oxidation is the most extensively used method. A significant increase in the number of strong acidic groups like carboxylic groups was observed during oxidation by nitric acid [16]. The surface modified carbon has numerous applications as adsorbents and catalysts [17, 18].

The aim of the present study was to investigate the influence of nitric acid oxidation on the surface properties of low cost wheat and barley straw carbons. The effects of surface modifications on the properties of the carbons were studied in terms of the specific surface area, FT-IR, total number of acidic groups, PZC and TG-DTA analysis. The adsorptive properties of the carbons before and after modification were also studied for the adsorption of Cr(III) ions.

6.2. Experimental

6.2.1. Carbonization of straw. The carbonization process is discussed in section 2.2.1. of Chapter 2. In this case carbon prepared at 800°C has been used.

6.2.2. Oxidation of carbon. The CWS and CBS were oxidized at 90°C using 50% nitric acid. The reaction mixture was heated to 90°C and the reaction was allowed to continue for 6 h with continuous stirring. The used reaction solution was discharged and a fresh reaction mixture of 50% nitric acid was added. The reaction was allowed to continue for a further 3 h under the same reaction conditions. The oxidized carbons were then filtered and washed with distilled water till neutral pH. The samples were then dried in a convection oven at 50°C for 24 h and used in the experimental work under the following names: the oxidized carbonized barley straw (OCBS) and the oxidized carbonized wheat straw (OCWS).

6.2.3. Characterization of carbon. Physical gas adsorption is an extensively used technique in the characterization of porous materials which accurately determines the surface area, pore volume and pore size distribution. The adsorption of such gases as N₂, Ar and CO₂ is frequently used for this purpose. In this case N₂ adsorption at 77K was carried out using a Belsorp 18PLUS-SP (BEL. JAPAN. INC.). Before measuring the adsorption of N₂, the sample was subjected to degassing for 3 h at 300°C to a final pressure of 0.1 Pa. The N₂ adsorption-desorption isotherms were analyzed to characterize the nature of the pores. BET-Plots and t-Plots were analyzed to calculate the specific surface area and average pore diameter. The classical pore size model developed by Barret, Joyner and Halande (BJH) was used for the pore size distribution

calculation.

6.2.4. Thermogravimetric – differential thermal (TG-DTA) analysis. Simultaneous thermogravimetric – differential thermal analysis was performed on the oxidized and unoxidized carbon materials using a TG/DTA 6300 (Seiko Instruments Inc.). About 5 mg of each sample were heated from 10 to 1000°C at a heating rate of 10 °C/min. The results provided both TG and DTA plots.

6.2.5. PZC. The pH value required to give zero net surface charge, designated the point of zero charge (PZC), was measured by a mass titration method [19]. Three solutions with different initial pH values were prepared using HNO₃ and NaOH, while NaNO₃ was used as the background electrolyte. For each initial pH value, six conical flasks were filled with 25 ml of the solution and different amounts of carbon were added so as to make the solid fraction 0.05%, 0.1%, 0.5%, 1%, 5% and 10%. The mixture was shaken for 24 h and the equilibrium pH was measured. The change in pH values as a function of the mass fraction of carbonized material in the solution (wt/v%) was plotted. The plot exhibits a plateau and the PZC was evaluated as the average of three asymptotic pH values. The carbon surface is positively charged below this pH and negatively charged above this pH.

6.2.6. Determination of the acidic surface functional group. The Boehm titration method [20] was used for the determination of the acidic surface functional groups on the carbon materials. A carbon sample, 100 mg, was placed in 25 ml of the following 0.05 M solutions: sodium hydroxide, sodium carbonate and sodium bicarbonate. The solutions were shaken for 24 h and then 5 ml of each filtrate was pipetted and excess of base was titrated with standard HCl. The number of various types of acidic sites was calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na₂CO₃, carboxylic and lactonic groups; and NaHCO₃, only carboxylic groups.

6.2.7. FTIR spectra analysis. The CWS, CBS and their oxidized forms before and after adsorption of Cr(III) were examined using a JASCO FT/IR-460 Fourier transform

infrared (FTIR) spectrometer. The discs were prepared by mixing 1 mg of powdered carbon with 100 mg of KBr. The spectra were recorded between 4000 and 1000 cm^{-1} .

6.2.8. Adsorption studies. The Cr(III) solution was prepared by dissolving analytical grade $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ p (Wako Pure Chemical Industries, Ltd.) in distilled water. The pH of the solution was adjusted using 0.1M HEPES buffer. Adsorption tests were performed by adding 25 mg of the adsorbent to 15 ml of the Cr (III) solution. The mixture was shaken in a thermostated shaker at 30°C. The suspended mixture was filtered through a filter paper and the equilibrium pH of the filtrate was measured using an ORION model 720A pH meter. The chromium concentration was measured using a Shimadzu Model ICPS-8100 ICP/AES spectrometer. The adsorption experiments were performed at different pH values, at different concentrations and at different contact time. All the experiments were conducted in triplicate and mean values are reported in this paper. The maximum standard deviation observed was less than 5%.

6.3. Results and discussion

6.3.1 Physical properties. The N_2 adsorption-desorption isotherms are shown in Fig. 6.1. The adsorption isotherms for all samples investigated were primarily of Type I, a characteristic of microporous materials. However, the small hysteresis loop in the adsorption-desorption isotherms indicates the existence of mesopores. When a solid contains very fine micropores, the potential force field from the neighboring walls of the pores will overlap causing an increase in the interaction energy between the solid surface and the gas molecules [7]. This will result in an increase in adsorption, especially at low relative pressures causing complete filling of the pores at quite a low relative pressure, giving rise to a Type I isotherm. These isotherms are thus characterized by a plateau exhibiting a small amount of adsorption at higher relative pressures. The pores are too narrow to accommodate more than a single molecular layer, and so the Type I isotherms do not increase continuously.

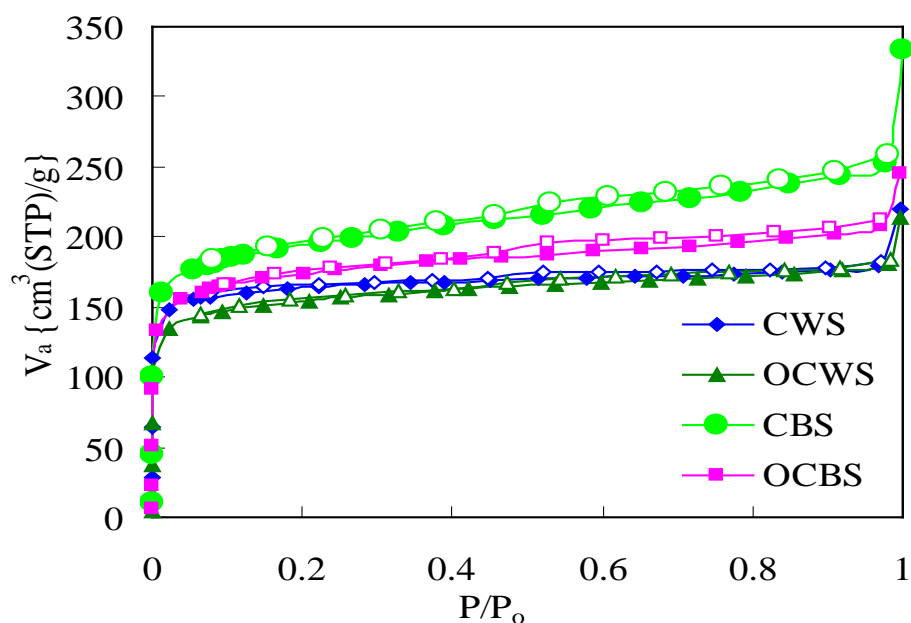


Fig. 6.1. Nitrogen adsorption (closed symbol) and desorption (open symbol) isotherms for carbons.

In the presence of mesopores, capillary condensation will occur during adsorption and is preceded by a metastable fluid state (“cylindrical meniscus”), while capillary evaporation during desorption occurs via a hemispherical meniscus, separating the vapor and the capillary condensed phase, which will result in hysteresis, since mesopores are filled at higher pressure and emptied at lower pressure [21].

The structural characterization results are listed in Table 6.1. The specific surface area was measured by means of a BET-Plot and a t-Plot. The mean of these two specific surface areas is given in Table 6.1. It can be seen that although no activation process was employed for preparation of carbon, yet the specific surface area of carbon is high enough to that of activated carbon. The specific surface area decreased after oxidation in both types of carbonized materials. The average pore diameter evaluated by the BET-Plot is also given in the same table.

Table 6.1. Variation in characteristics of carbonized straw after oxidation.

Carbon	Specific surface area (m ² /g)	Average pore diameter (nm)	Carboxylic functional group (mmol/g)	Phenolic functional group (mmol/g)	Lactonic functional group (mmol/g)	Total acidic group (mmol/g)	PZC
CWS	700	2.03	0.24	0.02	0.02	0.29	9.00
OCWS	636	2.13	2.84	0.66	0.64	4.14	2.45
CBS	792	2.52	0.12	0.07	0.07	0.27	9.20
OCBS	721	2.24	1.38	1.49	1.08	3.95	2.58

Figure 6.2 shows the pore size distribution of oxidized and unoxidized carbon materials, which suggests that carbon oxidation brings about a decrease in pore volume. This is attributable to the blockage of the pore entrances by the formation of humic substances during HNO₃ treatment [22]. The specific surface area of the oxidized materials has decreased for the same reason. The pore blockage occurs mainly in the microporous region but the mesoporosity structure remained mostly unchanged. In both types of oxidized and unoxidized carbonized wheat and barley straw samples, the narrow distribution of pores averaged around 1.22 nm as shown in Fig. 6.2, indicating that the nature of the porosity has not been altered by the oxidation. This is in good agreement with the average pore diameter of approximately 2 nm evaluated from the BET-Plot for all four types of carbons.

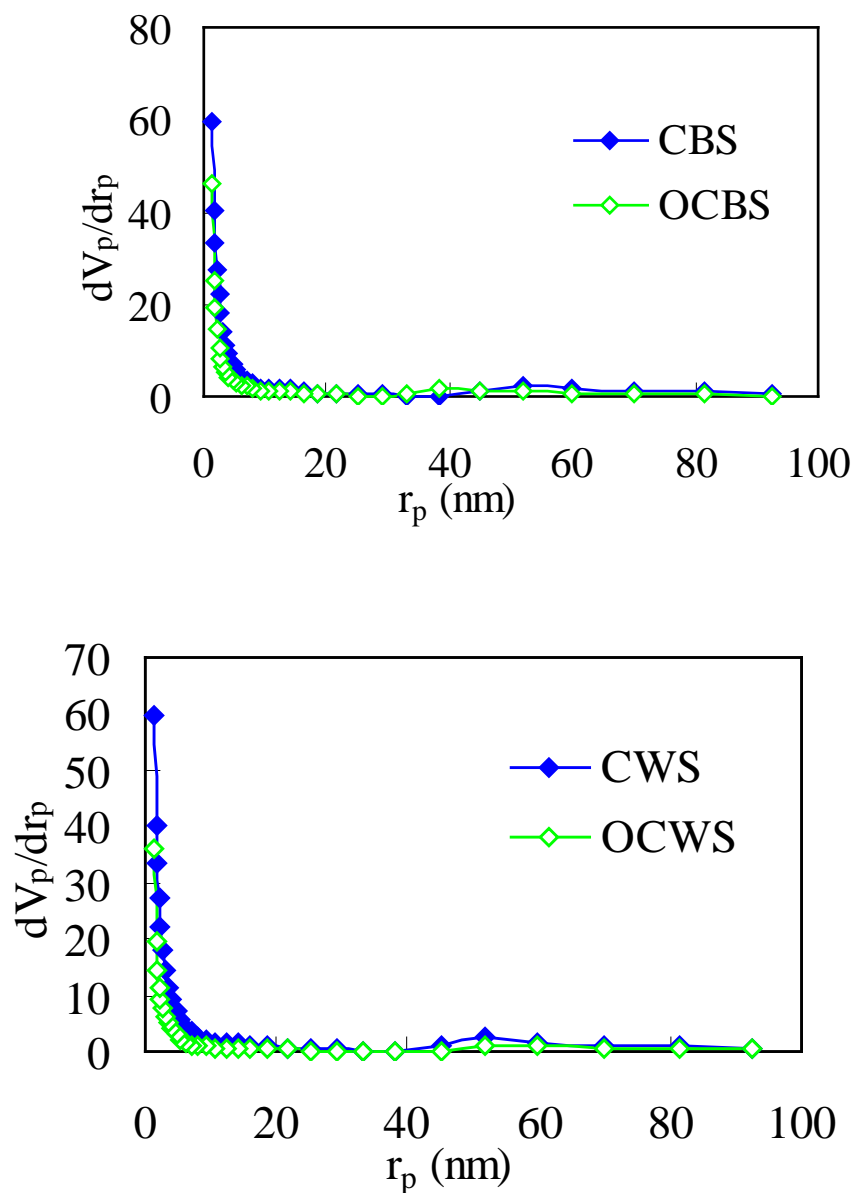


Fig. 6.2. Pore size distribution of the carbons.

6.3.2. TG-DTA. Figure 6.3. shows the TG and DTA plots for oxidized and unoxidized carbon samples. In both types of oxidized carbonized straw, weight loss commences quite early as shown by the peak in the DTA plot close to 70°C , indicating a higher affinity for water. In the case of the oxidized carbons, successive weight loss and decomposition commences quite early and their weight gradually decreased. In the case of the unoxidized carbon samples, weight loss in the lower temperature range is not marked but a sharp weight loss occurs near 500°C .

From the TG-DTA results, it can be deduced that wet oxidation of CWS and CBS

with HNO_3 leads to the formation of an appreciable degree of functionality on the carbon surface. These functionalities become attached to such a high degree that their removal, primarily as CO_2 requires high energy. CWS and CBS showed a rapid weight loss near 500°C while OCWS and OCBS showed a more gradual weight loss that extended up to 600°C even though the weight loss commenced at low temperature, which reflects the relative thermal stability of the oxidized sample compared to the unoxidized samples. It can be concluded from the TG analysis that the different nature of weight changes monitored up to 1000°C reflects the successful functionalization of CWS and CBS using 50% HNO_3 .

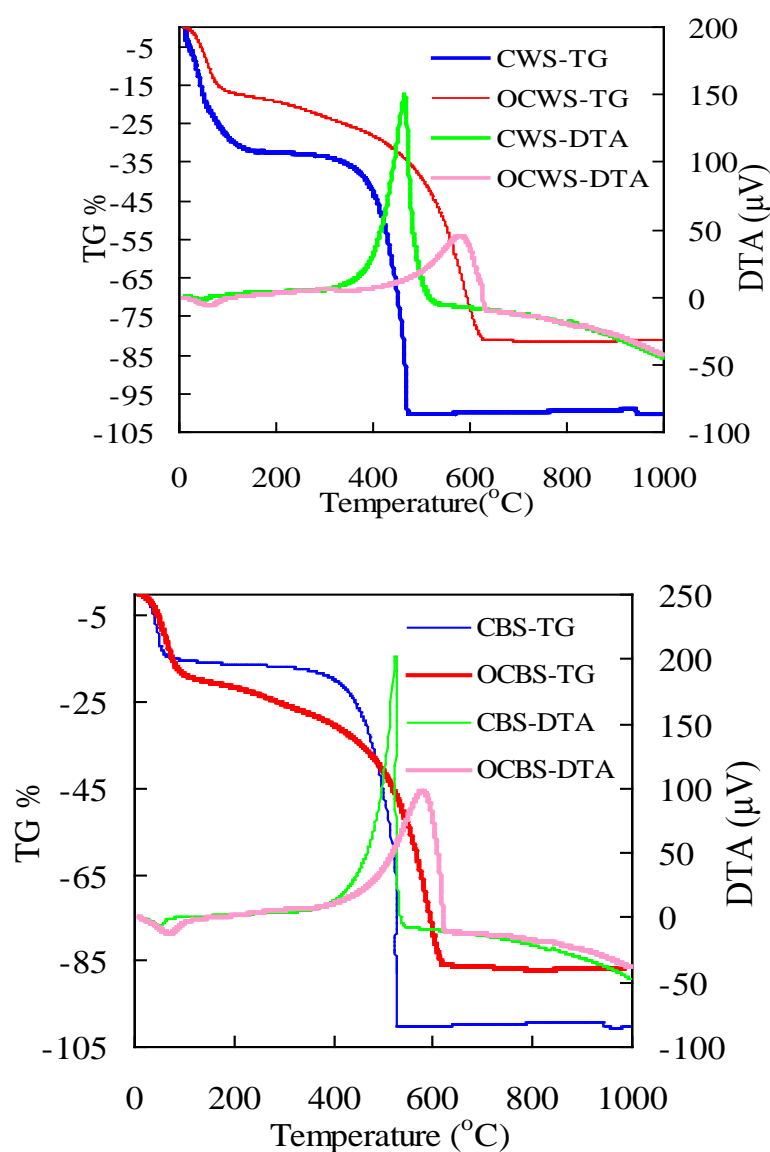


Fig. 6.3. TG-DTA curves.

6.3.3. PZC. The PZC values of the samples are shown in Table 6.1. The PZC values of unoxidized carbons are basic, whereas after oxidation using HNO_3 , they become acidic. It is known that oxidation of carbon with HNO_3 induces a significant amount of carboxylic, lactonic and phenolic groups on the carbon surface [16] due to which causes the PZC values to shift from pH 9.00 and 9.20 down to pH 2.45 and 2.58 after the oxidation for CWS and CBS, respectively.

6.3.4. Boehm titration. The results of the Boehm titrations are listed in Table 6.1. The titration results suggest that all the carbon samples possess oxygen functionalities in the form of carboxylic, lactonic and phenolic groups. The content of strongly acidic carboxylic groups is substantially increased by oxidation. Modification by oxidation increased the total acidity by 13.9 and 14.2 fold in the case of CWS and CBS, respectively. The results show that the carboxylic surface group content, which is very low in the unoxidized carbon samples, has been increased by 11.5 and 11.3 fold by the oxidation in CWS and CBS, respectively.

6.3.5. Fourier transform infrared spectroscopy. Figure 6.4. shows the FTIR spectrum of CWS, CBS and their oxidized forms before and after adsorption of Cr(III). Observation of the absorption bands shows that the changes between the oxidized and unoxidized carbons are mainly due to the formation of oxygen functionalities. The most characteristic changes are observed in the $1800\text{-}1000\text{ cm}^{-1}$ range. The band centered at 1750 cm^{-1} is usually ascribed to the stretching vibration of $\text{C}=\text{O}$ in ketones, aldehydes, lactones, and carboxyl groups. The band around 1600 cm^{-1} is attributed to COO^- asymmetric stretching. The appearance of these peaks after oxidation indicates the formation of new oxygen functionalities or an increase in the already existing oxygen functionalities. The broad adsorption band in the $1300\text{-}1000\text{ cm}^{-1}$ range can be assigned to various C- bonds, such as those in ethers, phenols and hydroxyl groups. These results indicate that HNO_3 treatment give rise to a large increase in carboxylic and lactone group $\text{C}=\text{O}$ bonds, resulting in the increased surface acidity of the carbonized materials.

The sites responsible for the adsorption of cation is due to the $-\text{COOH}$ groups which has strong complexing properties forming heterocyclic chelates with M^+ ions depending on the pH of liquid phase [23]. Peaks at 1400 cm^{-1} appears after adsorption

of Cr(III) on OCWS and OCBS which was due to formation of ester like groups. Cr³⁺ ions adsorb on the carbon surface forming heterocyclic chelates with –COOH groups. This will create an ester like groups which is supported by the appearance of peak at 1400 cm⁻¹ after adsorption of Cr(III) on OCWS and OCBS in Fig. 6.4.

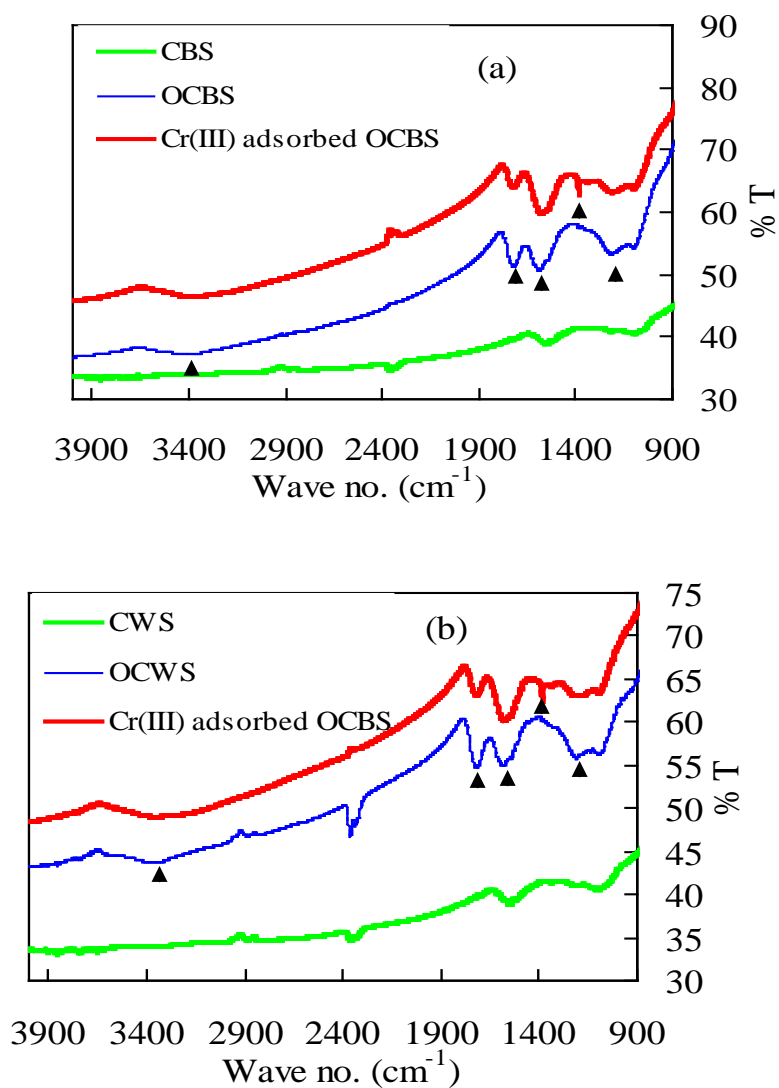
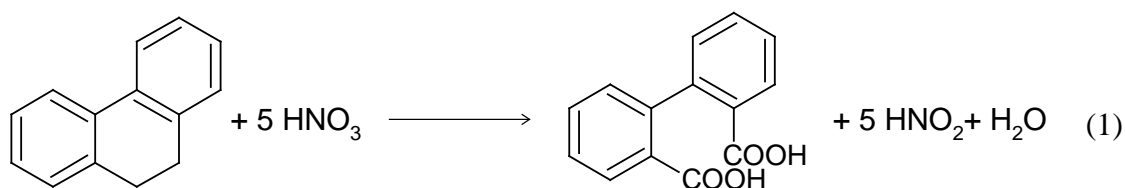


Fig. 6.4. Fourier transform infrared (FT-IR) spectrogram.

The results of Boehm titrations and FTIR analyses suggest that the number of carbonyl groups, of which there are very small amounts initially in the carbonized materials, was increased by oxidation with nitric acid. As described by Chingombe *et al.* (22), carbon materials consist of condensed aromatic structures. In the case of modification by oxidation, the reaction is most likely to occur on the aliphatic side chains of aromatic rings because such sites are highly susceptible to oxidation as shown

in (1).



6.3.6. Effect of the pH on adsorption of Cr(III). Figure 6.5. shows the effect of pH on the adsorption of Cr(III) on oxidized and unoxidized carbon samples. The adsorption of Cr(III) was tested over a pH range of 1-5. At pH values higher than 5, adsorption tests were difficult due to the formation of chromium hydroxide precipitates. The % adsorption of Cr(III) increases with increasing pH, suggesting that the adsorption takes place according to a cation exchange mechanism, which is considered to be caused by the abundance of carboxylic functional groups on the carbon surface.

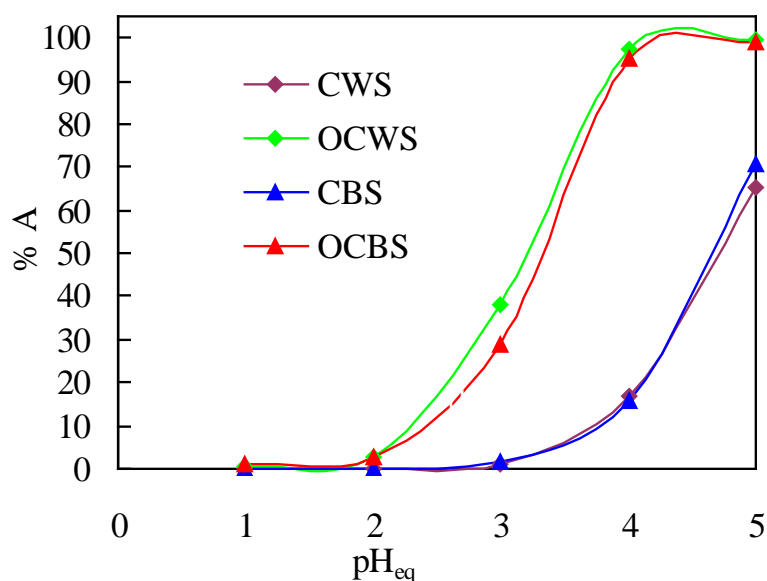


Fig. 6.5. Effect of equilibrium pH on the adsorption of Cr(III) on carbons. Weight of adsorbent= 25 mg; Volume of Cr(III) solution= 15 ml; Initial concentration of Cr(III)= 0.5 mmol/L; Shaking time= 24 h.

In Fig. 6.5., the pH at which the adsorption of Cr(III) takes place is shifted to lower pH values by about 1.5 pH units between the oxidized carbon materials and the unoxidized ones, which is attributed to the increase of carboxylic groups by the nitric

acid oxidation in agreement with the results of the Boehm titrations.

6.3.7. Adsorption isotherms. Figure 6.6. shows the adsorption isotherms for Cr(III) on the tested samples at pH 5. The amount of adsorption increases rapidly with increasing Cr(III) concentration at low Cr(III) concentrations and slowly reaches a constant value corresponding to each sample at high Cr(III) concentrations, as expected for Langmuir-type adsorption curves. From the constant values, the maximum adsorption capacities were evaluated as 0.30, 1.00, 0.29 and 0.93 mmol/g for CWS, OCWS, CBS and OCBS, respectively, suggesting that oxidation has increased the maximum adsorption capacity by 3.33 and 3.20 times for CWS and CBS, respectively, which can be correlated to the increases in the density of carboxylic groups on the surface of CWS and CBS.

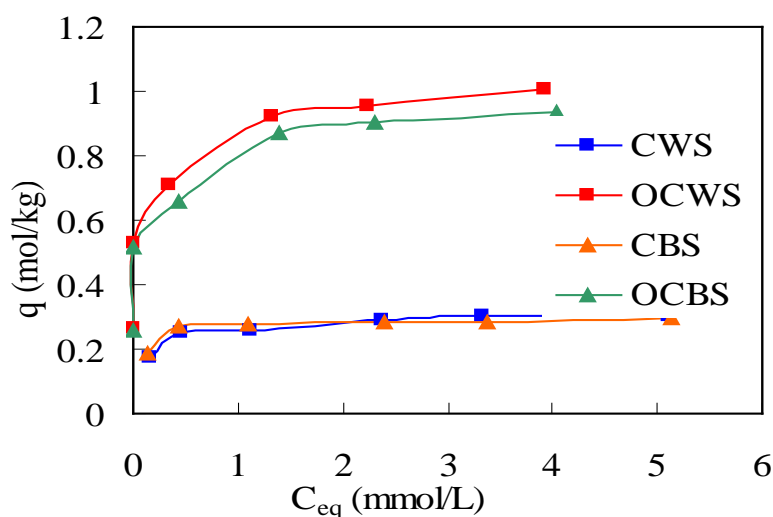


Fig. 6.6. Adsorption isotherms for Cr(III) on carbons. Weight of adsorbent= 25 mg; Volume of Cr(III) solution= 15 ml; Shaking time=24 h; pH= 5.

Table 6.2. lists the result of the Langmuir plot for the data shown in Fig. 6.6. The Langmuir equation is represented as follows [24]:

$$1/q_e = 1/\theta \cdot b \cdot C_e + 1/\theta \quad (2)$$

where C_e is the equilibrium concentration (mmol/L) and q_e the amount adsorbed at equilibrium (mmol/g). The Langmuir constants, θ and b , which are related to the adsorption capacity and heat of adsorption, respectively were calculated as listed in

Table 6.2. The high correlation coefficients as shown in Table 6.2. suggests that the Langmuir isotherm well describes the Cr(III) adsorption.

Table 6.2. Estimated Langmuir isotherm parameters for Cr (III) adsorption at 30°C and at pH 5.

Langmuir isotherm equation	Estimated isotherm parameters		
	R^2	θ	b
$1/q_e = 1/\theta.b. C_e + 1/\theta$			
CWS	0.98	8.54	0.30
OCWS	0.93	142.05	0.93
CBS	0.97	128.51	0.29
OCBS	0.96	44.44	0.85

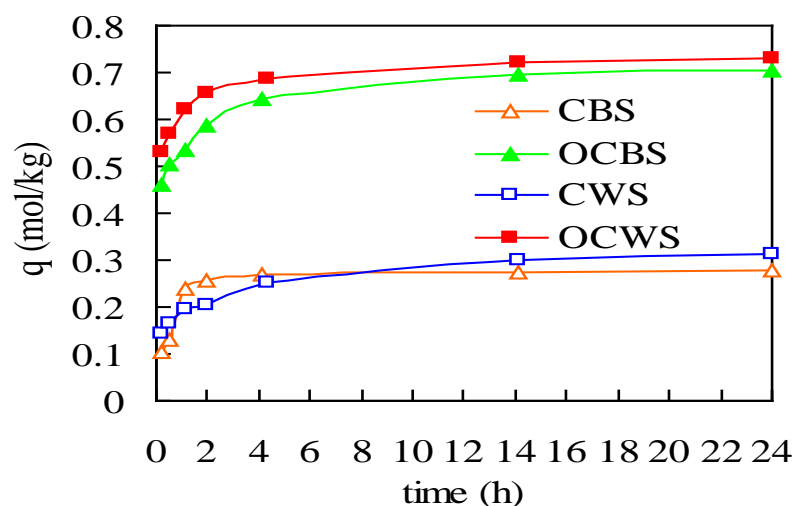


Fig. 6.7. Effect of contact time on adsorption of Cr(III) on carbons. Weight of adsorbent= 25 mg; Volume of Cr(III) solution= 15 ml; Initial concentration of Cr(III)= 2 mmol/L; pH= 5.

6.3.8. Effect of contact time. Figure 6.7. shows the effect of contact time on the adsorption of Cr(III) on carbons. It shows that the rate of adsorption on all type of carbons studied were very fast and equilibrium was achieved within 4 h contact time. The very fast kinetic and enhanced adsorption capacity makes oxidized CBS and CWS more preferable adsorbent.

6.3.9. Comparison of the oxidized carbon with other adsorbents. Table 6.3. summaries the comparison of the maximum adsorption capacities for various adsorbents for Cr(III) reported in the literature including the oxidized carbons in this work. It can be seen that the carbon produced after oxidation of carbonized barley and wheat straw by a simple process are superior to many other adsorbent for trivalent chromium adsorption, indicating that it can be promising alternative for Cr(III) ion removal from industrial effluent. The significantly high adsorption capacities of these adsorbents are attributable to introduction of acidic functional group by oxidation method.

Table 6.3. Comparison of the maximum adsorption capacity for Cr(III) on different adsorbents.

Adsorbent	pH	Temperature (°C)	Adsorption capacity [mmol/g]	Reference
Activated carbon	5.0	25	0.76	[25]
Diatomite	6.0	30	0.54	[26]
Lignin	5.0	20	0.34	[27]
Lignite based humic acid	4.1	20	0.29	[23]
Turkish brown coal	4.5	25	0.26	[28]
Zeolites		28	0.05	[29]
OCWS	5.0	30	1.00	This work
OCBS	5.0	30	0.93	This work

6.4. Conclusions

The chemical modification employed in the present work only slightly changed the specific surface area but significantly changed the surface chemical structure. Acidic surface functional groups were introduced by nitric acid oxidation, which was

confirmed by FTIR analysis and measurement of surface functional groups by means of the Boehm method. The decrease in PZC after oxidation also supports the fact that acidic groups have been introduced. The surface modification produced carbon samples with a very different chemical nature but a similar porous structure. As shown by the BJH plots, the pore size distribution is almost the same before and after the oxidation. The only difference was a small decrease in the volume of the pores, which was also verified by the nitrogen adsorption-desorption isotherms, suggesting that the carbon materials maintain a microporous structure even after oxidation. However a slight decrease in the surface area took place after oxidation. The adsorption tests for Cr(III) at different pH values and Cr(III) concentrations showed that the oxidized straw carbons exhibit a high efficiency for Cr(III) ions in comparison to the unoxidized carbons. Thus the carbon materials prepared from waste straw can be modified into good cation ion exchanging adsorbents by the simple method of oxidation.

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CONCLUSION

The increasing industrialization has intensified environmental pollution and the deterioration of ecosystems, with the accumulation of pollutants such as heavy metals, synthetic compounds *etc.* Water and wastewater contaminated by heavy metals have an adverse impact on public health and economy, and exposure to heavy metals even at trace levels is believed to be a risk for human health. Considering its hazardous risks for human health, the treatment of industrial effluents to reduce or remove the pollutant before discharge into the environment becomes inevitable.

The expanded use of electronic devices and the rapid technology change has led to significant increase of electronic and electrical wastes, popularly known as e-waste. It is the fastest growing waste flows worldwide. E-waste contains both valuable materials (Au, Ag, Pd, Pt, Cu, *etc.*) as well as hazardous materials (Pb, Hg, Cd, As, *etc.*) which require special handling and recycling methods. Since the amounts of precious metals and their mining are very limited throughout the world, the recovery of precious metals from such secondary sources is in high demand.

In the past decades various processes have been developed to treat such wastes to separate toxic and valuable materials among which adsorption using activated carbon is most widely used. Activated carbons are versatile adsorbent due to their extended surface area, high adsorption capacity, microporous structure and special surface reactivity. The consumption of activated carbon is ever increasing due to increasing industrialization and pollution. Since carbon sources are rather limited or very expensive, production of carbon materials from agricultural wastes is required. Their advantage as carbon feedstock includes abundant availability and renewability, low cost and good quality carbon generation. Considering this fact low cost porous carbon was prepared using agrowaste such as rice husk, wheat straw and barley straw and their performance for metal ions adsorption was investigated. The following conclusions have been drawn from the experimental results:

1. High surface area porous carbons are prepared from agrowaste using simple single step carbonization method where the only thing that is wasted is electricity.
2. At 800°C carbonization temperature the carbon produced has high specific surface area as well as good % yield thus it is the optimum carbonization temperature.
3. Wheat straw and barley straw are found to be good raw materials in comparison to rice husk because of generation of porous carbon with low ash content and high specific surface area.
4. The carbon prepared is mainly microporous with positively charged surface at acidic pH. Thus adsorption of metal ion such as Cr(VI), Au(III), Pt(IV) and Pd(II) which exist in anionic form in aqueous solution was investigated.
5. Because of its positively charged surface and high specific surface area carbonized

barley straw and carbonized wheat straw effectively remove Cr(VI) ion from acidic solution, exhibiting maximum adsorption capacities of 1.68 and 1.67 mol/kg for total chromium, respectively at pH 2. The equilibrium was reached within 1 h of contact time. The high adsorption capacity and very fast kinetic of both type of carbons studied make them promising alternatives for Cr(VI) removal.

6. Carbonized rice husk exhibit strong selectivity for Au(III), whereas carbonized barley and wheat straws are selective for all Au(III), Pd(II) and Pt(IV) over various base metals. All these carbons have no affinity for other contaminating metal ions like Cu(II), Fe(III), Ni(II) *etc.*
7. The adsorption of Au(III) on all adsorbents is nearly independent of hydrochloric acid concentration, which is advantageous in practical applications. The very fast metal ion adsorption rate of barley and wheat straws carbon is an additional advantage.
8. The porous carbons have very high adsorption capacities for gold comparative to Palladium and platinum. The enhanced adsorption capacity for Au(III) is due to Au(III) to Au(0) reduction after adsorption. In 1 M hydrochloric acid medium, the maximum adsorption capacities of carbonized materials are observed as:

Carbonized	Au(III) (mol/kg)	Pd(II) (mol/kg)	Pt(IV) (mol/kg)
Rice husk	0.78	-	-
Barley straw	1.49	0.62	0.39
Wheat straw	1.15	0.40	0.19

9. The wheat straw carbon was also studied for adsorption in continuous mode and found to be suitable for it. The maximum adsorption capacity for Au(III) in continuous mode at 1 M HCl concentration was 1.01 mol/kg, which is very high in comparison to other adsorbent studied in literature. The high adsorption capacity of Au(III) in column test was attributed to its fast kinetics.
10. The carbonized materials show less affinity for metal ions that exist in cationic form. Thus chemical modification of the carbonized wheat straw and barley straw was done using nitric acid, which only slightly changed the specific surface area but significantly changed the surface chemical structure. Acidic surface functional groups were introduced by nitric acid oxidation, which was confirmed by FTIR analysis, measurement of PZC and surface functional groups. The adsorption tests for Cr(III) at different pH values and Cr(III) concentrations showed that the oxidized straw carbons exhibit a high efficiency for Cr(III) ions in comparison to the unoxidized carbons.

List of Publications

1. Rumi Chand, Takanori Watari, Katsutoshi Inoue, Toshio Torikai, Mitsunori Yada, Evaluation of Wheat Straw and Barley Straw Carbon for Cr(VI) Adsorption, Separation and Purification Technology 65 (2009) 331-336.
2. Rumi Chand, Takanori Watari, Katsutoshi Inoue, Hom Nath Luitel, Toshio Torikai, Mitsunori Yada, Chemical modification of carbonized wheat and barley straw using HNO₃ and the adsorption of Cr(III), Journal of Hazardous Materials 167 (2009) 319-324.
3. Rumi Chand, Takanori Watari, Katsutoshi Inoue, Hidetaka Kawakita, Hom Nath Luitel, Durga Parajuli, Toshio Torikai and Mitsunori Yada. Selective adsorption of precious metals from hydrochloric acid solutions using porous carbon prepared from barley straw and rice husk, Minerals Engineering (2009) doi:10.1016/j.mineng.2009.07.007.
4. Rumi Chand, Takanori Watari, Katsutoshi Inoue, Hom Nath Luitel, Hidetaka Kawakita, Toshio Torikai, Mitsunori Yada, Recovery of precious metal using wheat straw carbon, Journal of Hazardous Materials (under review).
5. Rumi Chand, Takanori Watari, Toshio Torikai, Mitsunori Yada and Katsutoshi Inoue. Adsorption behavior of barley straw carbon for chromium (VI) ion, Materials Science Forum 569 (2008) 213-216.
6. Rumi Chand, Kenji Narimura, Hidetaka Kawakita, Keisuke Ohto, Takanori Watari and Katsutoshi Inoue. Grape waste as a biosorbent for removing Cr(VI) from aqueous solution, Journal of Hazardous Materials 163 (2009) 245-250.
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8. Takanori Watari, Rumi Chand, Daisuke Tomita, Toshio Torikai and Mitsunori Yada. Preparation of porous carbon from bio-treated orange waste, The 24th International Japan-Korea Seminar on Ceramics November, 2007. Kakegawa, Shizuoka, JAPAN.

Contribution to Conferences

1. Rumi Chand, Takanori Watari, Toshio Torikai, Mitsunori Yada and Katsutoshi Inoue. Preparation of barley straw carbon and its evaluation for Chromium(VI) adsorption. *The 5th Japan/Korea International Symposium on Resources Recycling and Materials Science*. **December, 2007**. Kitakyushu University, Kitakyushu, JAPAN.
2. Rumi Chand, Takanori Watari, Toshio Torikai, Mitsunori Yada and Katsutoshi Inoue. Adsorption behavior of barley straw carbon for chromium (VI) ion. *The 9th International Symposium on Eco-materials Processing and Design*. **January, 2008**. Kyungnam University, Changwon-city, KOREA.
3. Rumi Chand, Takanori Watari, Toshio Torikai, Mitsunori Yada and Katsutoshi Inoue. Evaluation of chromium(VI) adsorption on wheat straw and barley straw carbon. *The 1st Saga University and Daegu University Joint Seminar New Trends in Chemistry and Biology*. **January, 2008**. Saga University, Saga, JAPAN.
4. Rumi Chand, Takanori Watari, Katsutoshi Inoue, Hidetaka Kawakita, Toshio Torikai, Mitsunori Yada. Barley straw carbon as potential adsorbent for selective removal of precious metal ion. *The 21st International Symposium on Chemical Engineering*. **December, 2008**. Saga University, Saga, JAPAN.
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Area of Research Material Engineering for Separation: Recovery of metal ions using carbonized biomass

List of Major Publications

- R. Chand, et al. Sep. Pur. Tech., 65 (2009) 331-336.
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R. Chand, et al. J. Hazard. Mater. 163 (2009) 245-250.
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R. Chand, et al. Min. Eng. (2009) doi:10.1016/j.mineng.2009.07.007.

Reference

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