STUDY TO ADSORBENT OF RICE HUSK & SAW DUST (AGRICULTURE WASTE & TIMBER WASTE)

*MOHMMAD SUBHAN, #DR. PARDEEP

*Ph.D. Research Scholar (Civil engineering)

#Professor, H.B.I.T. KANPUR

ABSTRACT

In this study Agriculture waste (Rice husk) and timber industry waste (Saw dust) were selected for the making of adsorbent. Because of their easily availability, low cost, easy preparation, handing and storage make them suitable low cost biosorbents. The removal of three metal pollutants commonly encountered in electroplating effluents namely- Chromium, Nickel and Copper has been investigated.

The objectives of this study were:

1.   Preparation and characterization of biosorbents using rice husk and saw dust.

2.   To explore the adsorption efficiency of different biosorbents under different experimental conditions including pH, biosorbents dose, initial metal ion concentration, contact time and temperature in batch mode experiments and in mono, binary and multi-metal systems.

3.   Application of different isotherms to the generated data.

4.   Desorption studies to explore the reuseability of the biosorbents.

5.   Removal of heavy metals from industrial effluent under optimum experimental conditions.

INTRODUCTION

Heavy metals can be defined on the basis of their physical, chemical and biological properties. The term heavy metal is somewhat imprecise and refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). Passow et al (1961); Hutton and Symon (1986); Nriagu and Pacyna (1988) and Hawkes (1997) have defined heavy metals as general collective term, which applies to the group of metals and metalloids with density greater than 5 g cm^{-3} and these includes elements from Group III transition metals, the actinides series, the lanthanide series and three of the Group IV metalloids (arsenic, tellurium, selenium). Heavy metals are classified into three categories on the basis of their usage in the field of biosorption (Volesky, 1990; Bishop, 2002):

- Toxic metals (such as Hg, Cr, Pb, Zn, Cu, Cd, As, Co & Sn)
- Precious metals (such as Pt, Ag, Ni, Au & Ru)
- Radionuclides (such as U, Th, Ra & Am)

Heavy metals interaction with water exist in two forms

Water-soluble

Chloride, sulphate and nitrates salts of heavy metals are water soluble. These are most common salts of heavy metal ions used in industrial operations. As a dissolved salt, heavy metal ions are in cationic form such as Cd^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Cr^{3+}. Heavy metals can also exist in soluble form as oxymetal anions like chromium, which can also exist as chromate CrO_4^{2-} or dichromate $Cr_2O_7^{2-}$. Another example is arsenic, including arsenate (AsO_4^{3-}), which has an oxidation state of +5, arsenite (AsO_3^{3-}), where As has oxidation state of +3, as well as selenium (SeO_2^{3-}, SeO_4^{2-}) (Stephengen and Lester, 1987).

Water-insoluble

Oxide, hydroxide, sulphide and carbonate salts of most heavy metals are not soluble or are sparingly soluble in water.

SOURCES OF HEAVY METALS

Rapid increase in world population and industrialization has seriously contributed heavy metal pollution of ecosystem. Heavy metals are present in marine, ground and industrial wastewater (Nuhoglu et al, 2002). Heavy metals enter into the environment by both natural and anthropogenic sources. Major sources of heavy metals into environment are geological weathering and industries including mining and smelting of metalliferous & surface finishing industry, energy and fuel production, dyes and pigments, fertilizer and pesticide industry, electroplating, electrolysis, electro-osmosis, leather working, film and photography, electric appliances manufacturing, metal surface treating, aerospace and atomic energy installation (Niyogi et al, 1998). In addition, domestic effluents, landfill leachate, agricultural runoff and acid rain also contribute to heavy metals in water (Aksu and Kutsal, 1990). Heavy metals are often present together with organic pollutants in industrial wastewater (Lodi et al, 1998). Waste containing metals are directly or indirectly discharged into the environment increasingly, especially in developing countries, are a serious cause of environmental pollution and threatening aquatic life (Bishop, 2002; Volesky, 1990).

HEALTH IMPACT OF HEAVY METALS

For nearly a century, heavy metal-laden wastewater discharged from industries, are posing a serious challenge to environmental, public health, scientists and Engineers. Numerous investigations on effects of heavy metal on environment and human have been carried out. Unlike organic pollutants, which in most cases can be destroyed, heavy metal discharged into environment tend to persist indefinitely, circularly and eventually throughout the food chain thus causing a series of threats to human and organisms (Cooke et al, 1990; Deniseger et al, 1990; Sag et al, 1995b; Chua and Hua, 1996). Even if the heavy metal ions in water present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that

through natural processes, such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics (Atkinson et al, 1998).

Some of toxic characteristics of heavy metals are given below:

1. Toxicity can last for a long time.
2. Some heavy metals even could be transformed from relevant low toxic forms to more toxic forms in a certain environment, chromium is such a case; metals can only be transformed and changed in valence and species, but cannot be degraded by any methods including biotreatment.
3. Bioaccumulation of heavy metals by food chain can damage normal physiological activity and endanger human life.
4. The toxicity of metals occurs even in low concentration of about 1.0-10.0 mg L^{-1}.

EMISSIONS TO THE ATMOSPHERE

Heavy metals enter into the environment by both natural and anthropogenic sources. Emission levels of some of the heavy metals to the environment by different industrial and natural sources are given in Table 1.3. It is evident from the data that for several metals anthropogenic emissions to the air are significantly higher than natural emissions. A measure of the industrial influence on metal global cycling is the *interference factor* (IF) which is defined as the ratio of the natural to the industrial emission (Lantzy and Mackenzie, 1979).

Characteristics

Chromium is a naturally occurring element and widely distributed in the environment in several forms. Chromium, the 17th most abundant element on earth, is considered as one of the priority pollutants in the developing countries and elsewhere. Its atomic number is 24 and atomic weight is 52.01. Chromium was first discovered in the Siberian red lead ore (crociote) in 1798 by the French chemist Vauqnelin. It is a transition element located in the group VI-B of the periodic table with a ground-state electronic configuration of $[Ar]3d^54s^1$. Chromium is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is odourless, tasteless and highly resistant to corrosion. Naturally occurring chromium is composed of three stable isotopes; Cr^{52}, Cr^{53} and Cr^{54} with Cr^{52} being the most abundant (83.78% natural abundance).

Chromium majority exists in two oxidation states, Cr(III) and Cr(VI). The oxidation state of chromium compound and its solubility in aqueous solution are particularly important due to its toxicological effects on environment (Katz and Salem, 1994). Both Cr(III) and Cr(VI) compounds are found in nature, but the trivalent state chromium is most stable and abundantly available in the nature. The solubility of Cr(III) compounds is limited by the formation of several oxide and hydroxide species (Cainelli and Cardillo, 1984). Cr(III) salts give a green to blue color to aqueous solution (Saner, 1980). Cr(III) is less mobile, less toxic and is mainly remain bonded to organic matter in soil and aquatic environment (Becquer et al, 2003). The hydrolysis

behavior of Cr(III) is complicated and it produced mononuclear species $CrOH^{2+}$, $Cr(OH)_2^{+1}$, $Cr(OH)_4^-$, neutral species $Cr(OH)_3^\circ$ and poly-nuclear species (Mohan et al, 2005).

The solubility equilibrium of hexavalent chromium compounds is complex and pH dependent. In comparison with trivalent chromium compounds, Cr(VI) is more soluble under most environmental conditions. In acid media, hexavalent chromium compounds are strong oxidizing agents. At low pH, Cr(VI) is readily reduced to Cr(III) whereas at high pH, trivalent chromium is readily oxidized to the hexavalent state. The most prevalent form of chromium is hexavalent. It is more toxic than trivalent form of chromium as determined by the National Toxicological Programme (NTP). The International Agency for Research on Cancer (IARC) reported that Cr(VI) is human carcinogen. The Cr(VI) represented by chromates and dichromates which give yellow colour to aqueous solution and strongly acidic.

In nature, the cationic, trivalent chromium hydroxide, $[Cr(OH)]^{2+}$ is strongly adsorbed by suspended matters. Positively charged mineral particulates are able to adsorb the anionic, hexavalent chromium, CrO_4^{2-}. The mobility of hexavalent chromium in groundwater is significantly greater than trivalent chromium (Katz and Salem, 1994).

SOURCES OF CHROMIUM

Chromium is the naturally occurring element which is found in the volcanic-ash, volcanic-gases, soil and rocks (Abbasi and Soni, 1985). Chrome plating, leather tanning, combustion of natural fuels (gas, oil, coal), cement industries, catalysts, fertilizers, dye-manufacturing industries, batteries making, printers, emission from cooling towers, air condensers and incineration of sewage sludge, municipal refuse and other solid wastes, are the anthropogenic sources of chromium emission in the environment (Faisal and Hasnain, 2004). More than 1,70,000 metric tonnes of chromium wastes are discharged annually in environment as a result of industrial and manufacturing activities (Abassi et al, 1998). The leather industry is the major cause for the high influx of chromium to the biosphere, accounting for 40% of the total industrial use (Baruhart, 1997).

Chromium exists in food, air, water and soil, mostly in the trivalent form. It is only as a result of human activities that substantial amounts of Cr(VI) become present in environment. Cr(III) is comparatively insoluble while Cr(VI) is quite soluble and is readily leached from soil to groundwater or surface water.

REVIEW OF STUDIES

Biosorption of Fe(III), Cr(VI), Pb(II), Cu(II) and Ni(II) ions was examined on *Zoogloea ramigera* (activated sludge bacterium) and *Rhizopus arrhizus* (filamentous fungus) as a function of initial metal ion concentration and temperature by Sa and Kutsal (2000). Langmuir model was applied for each metal–microorganism system at different temperatures. The biosorption of Cu(II) and Ni(II) by both microorganisms was exothermic in nature. Whereas Fe(III), Cr(VI) and Pb(II) biosorption was an endothermic process.

Selvakumari et al (2001) studied the removal of Fe(II), Ni(II) and Cr(VI) metals from electroplating industry effluent by using maize corncob carbon. The optimum agitation time for Fe(II) removal was 90 min, whereas for Ni(II) and Cr(VI), the optimum time was 105 min; adsorbent dosages of 300 mg/50 ml for all metal ions; pH 6.0 – 7.0 was optimum for Fe(II) removal, pH > 9.0 for Ni(II) and 3.0 – 4.0 for Cr(VI).

Potential of two strains of *Dunaliella* algae for chromium (VI) biosorption from saline wastewater was tested by Gonul and Zumriye (2002). It was observed that uptake of chromium increased with increasing chromium concentration up to 250-300 mg L^{-1} and decreased rapidly with presence of increasing concentrations of salt for both the biosorbents. Maximum biosorption was at pH 2.0 by both the biosorbents.

Tiwari et al (2005) experimented for sorption and desorption of Cr(VI) using *Mucor hiemalis*. The biosorption capacity of biosorbents for Cr(VI) was 53.5 mg g^{-1} at pH 2.0. Desorption results showed that nearly 99% of Cr(VI) adsorbed on biosorbent was desorbed using 0.1N NaOH. Experiments on cyclic use of *M. hiemalis* showed that it retains its activity up to five sorption and desorption cycles.

Arslan and Pehlivan (2007) examined the ability of low-rank Turkish brown coals (Ilgın: BC_1, Beysehir: BC_2, and Ermenek: BC_3) for the removal of Cr(VI) from aqueous solutions and compared with the activated carbon from Chemviron (AQ-30). Adsorption of Cr(VI) was pH-dependent showing maximum uptake at equilibrium pH 2.3 for BC_1, 3.0 for BC_2 and 3.2 for BC_3 and AQ-30. Equilibrium results showed that maximum adsorption capacities were 7.81, 7.39. 4.80 and 3.10 mg g^{-1} for BC_3, BC_2, BC_1 and AQ-30 respectively.

Biosorption of Cr(VI) on *Termitomyces clypeatus* biomass has been reported by Das and Guha (2007). The optimum pH was 3.0. The amino, carboxyl, hydroxyl, and phosphate groups of the biomass were involved in chemical interaction with the chromate ion forming a cage like structure depicted by scanning electron microscopic (SEM) and Fourier transform infrared spectroscopic (FTIR) results. Based on desorption and FTIR studies it was concluded that Cr(VI) is reduced to Cr(III) on binding to the cell surface.

RESULTS & DISCUSSION

Detailed results and discussion of the experiments has been presented in this chapter. This chapter has been divided into following sections.

1.   Characterization of biosorbents
2.   Characterization of electroplating industry effluent
3.   Batch mode biosorption and its quantification
4.   Multi-metal biosorption studies
5.   Industrial feasibility of biosorbents

Characterization of biosorbents

Physico-chemical properties of biosorbents

Characterization of biosorbents were performed to obtain a better interpretation of the mechanism involved during the biosorption process and find out the changes in physico-chemical properties of native biosorbents after formaldehyde and sulphuric acid treatment. The physico-chemical properties of BRH (Boiled Rice Husk), FRH (Formaldehyde treated Rice Husk), RHC (Rice Husk Carbon), BSD (Boiled Saw Dust), FSD (Formaldehyde treated Saw Dust) and SDC (Saw Dust Carbon) biosorbents are given in Table 4.1 and Table 4.2.

On comparison of properties of the BRH, FRH and RHC biosorbents it was found that there is no significant change in bulk density, particle density and moisture content. The pH was 5.9 and 6.1 for the BRH and FRH which was slightly acidic. Where as pH of RHC was 4.3 which was more acidic than BRH and FRH. The electrical conductivity was 80, 110 and 160 µS cm^{-1} for BRH, FRH and RHC respectively. BSD, FSD and SDC also show similar kind of characters.

Table Physico-chemical characteristics of BRH, FRH and RHC biosorbents

Parameters	Biosorbent		
	BRH	**FRH**	**RHC**
pH	5.9	6.1	4.3
Electrical conductivity (µS cm^{-1})	80	110	160
Moisture content (%)	3.1	2.9	3.4
Bulk density (gm cc^{-1})	0.25	0.26	0.33
Particle density (gm cc^{-1})	0.37	0.38	0.40
Porosity (%)	32.43	31.58	17.50
Solubility in water (%)	4.23	6.12	8.45
Solubility in acid (%)	8.11	10.56	14.3

Table : Physico-chemical characteristics of BSD, FSD and SDC biosorbents

Parameters	Biosorbent		
	BSD	FSD	SDC
pH	5.6	5.9	4.4
Electrical conductivity (µS cm-1)	90	95	185
Moisture content (%)	2.1	2.4	3.8

| Bulk density (gm cc-1)	0.2	0.22	0.36
Particle density (gm cc-1)	0.31	0.32	0.42
Porosity (%)	35.48	31.25	14.32
Solubility in water (%)	5.45	6.78	9.87
Solubility in acid (%)	9.56	12.28	15.84

SEM and EDAX analysis of biosorbents

Scanning electron micrograph (SEM) and energy dispersive spectrum of X-ray (EDAX) were carried out for the biosorbents before and after equilibration. SEM helps in observation of changes in surface microstructures of the biosorbent. There are many studies which reported the utilization of the scanning electron microscopy analysis for showing the surface modification changes in the developed biosorbents (Lopez et al, 2003; Chun et al, 2004). The SEM microscopic pictures of native BRH, FRH, RHC, BSD, FSD and SDC and Cr(VI), Ni(II) and Cu(II) loaded biosorbents at 1000x magnifications are given in image 4.3 to image 4.26.

Scanning electron micrographs of native biosorbents (BRH and BSD) and after treatment with formaldehyde (FRH and FSD) and sulphuric acid (RHC and SDC) are shown in image 4.1 and image 4.2, which clearly indicate surface alterations in the biosorbents due to treatments. The surface features of the native BRH biosorbent reveal linear regular groove and ridges in fibrous network (image 4.1a) and native BSD show regular deep grooves and fine projections (image 1st).

The formaldehyde treated biosorbents (FRH and FSD) shows disrupted surface features. The distinct rupture structure visible in the electron micrograph indicated changes in the surface of biosorbents (image 1 and 2). The sulphuric acid treated biosorbents (RHC and SDC) on the other hand, improves the porous structure of the biosorbents with greater homogeneity, which can be clearly seen in the magnified view of the scanning electron micrograph (image 1st and 2nd).

Scanning electron micrograph of BRH surfaces before and after the biosorption of metals ion clearly shows the presence of Cr(VI), Ni(II) and Cu(II) ions (image 4.3 to image 4.6). Native BRH illustrated in image 4.3 showed irregular groove and ridges in fibrous network which is considered helpful for the accessibility of heavy metals to the biosorbent surface. The micrographs illustrated in image 4.4, 4.5 and 4.6 clearly indicated the presence of Cr(VI), Ni(II) and Cu(II) ions respectively, in the form of new shiny bulky particles and layer over the surface of metal loaded biosorbents (BRH) which are absent from the original biosorbent before loading metal ions shown in image 4.3. Similar kinds of results were observed for native and metals (Chromium, Nickel and Copper) loaded FRH (image 4.7 to 4.10), RHC (image 4.11 to 4.14), BSD (image 4.15 to 4.18), FSD (image 4.19 to 4.22) and SDC (image 4.23 to 4.26).
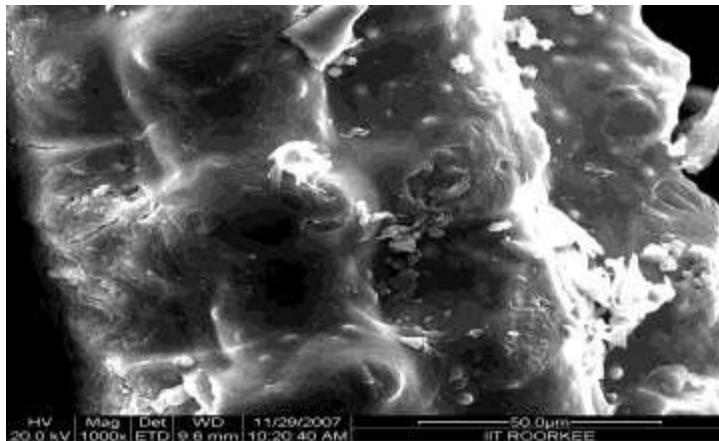
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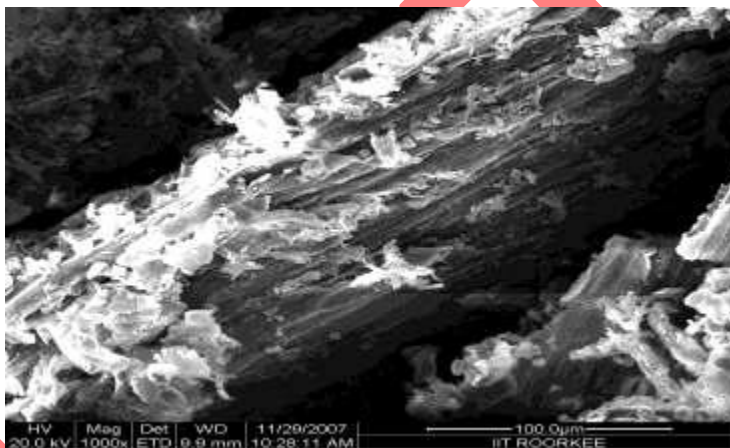
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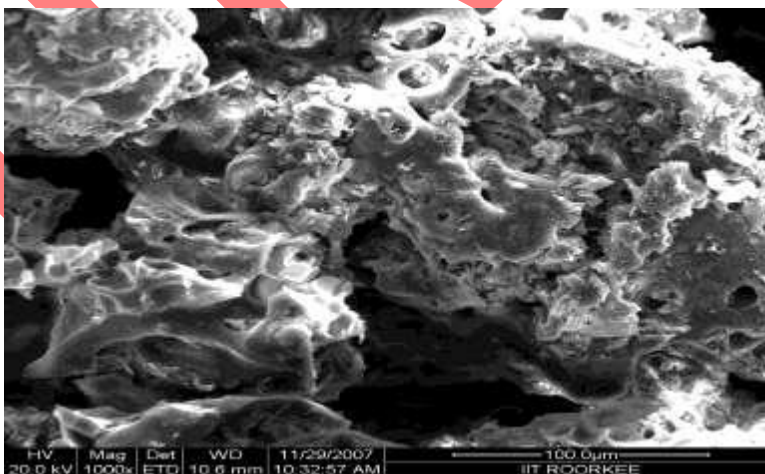
(C)

Image 4.1: SEM of Rice husk based biosorbents (A) Native, BRH (B) Formaldehyde treated, FRH (C) Sulphuric acid treated, RHC

CONCLUSION

The present study mainly focused on the develop of inexpensive and effective biosorbents for removing and recovering Cr(VI), Ni(II) and Cu(II).

The optimum pH, biosorbents dose, contact time and temperature for the removal of Cr(VI) from aqueous solutions were 2.0, 4 g L^{-1}, 120 min and 25^0C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Cr(VI) removal was in the order

SDC>RHC>FSD>FRH>BSD>BRH

The optimum pH, biosorbents dose, contact time and temperature for the removal of Ni(II) from aqueous solutions were 6.0, 20 g L^{-1}, 120 min and 25^0C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Ni(II) removal was in the order

RHC>SDC>FSD>BSD>FRH>BRH

The optimum pH, biosorbents dose, contact time and temperature for the removal of Cu(II) from aqueous solutions were 5.0, 20 g L^{-1}, 120 min and 25^0C respectively for all the studied biosorbents at low metal ion concentration. The efficiency of the studied biosorbents for Cu(II) removal was in the order

SDC>RHC>FSD>BSD>FRH>BRH

The maximum desorption of Cr(VI), Ni(II) and Cu(II) was recorded for BRH. The desorption of the studied metal ion from the exhausted biosorbents was in the order

Cu(II)> Cr(VI)>Ni(II)

The presence of other metals had antagonistic effect on the biosorption efficiency of the biosorbents. Further the metal removal efficiency of each biosorbent was lesser in actual effluent than aqueous solutions.

The biosorption pattern of all studied biosorbents studied followed the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm for biosorption of Cr(VI), Ni(II) and Cu(II). Kinetics results showed that all studied biosorbents for Cr(VI), Ni(II) and Cu(II) followed pseudo-second order model with determination coefficient (R^2) > 0.98.

Finally it was concluded that RHC and SDC were best biosorbents for the biosorption of studied metal ions. So rice husk and saw dust biosorbents can be attractive options for the small scale industries located in countryside. Rice husk and sawdust are readily available in developing nations, so this data can be used by small scale industries having low concentrations of Cr(VI), Ni(II) and Cu(II) in wastewater using batch or stirred-tank flow reactors where standard material, such as activated carbon, is not available.

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