IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)
e-ISSN: 2319-2402,p- ISSN: 2319-2399.Volume 14, Issue 2 Ser. I (February. 2020), PP 35-54
www.iosrjournals.org

Chromium Removal From Tannery Industry Waste Water By Fungus.

Khan Rajib Hossain.
Rajshahi University, Bangladesh.

Abstract: *Fungus has the ability to take up Chromium during the stationary phase of growth. Response of live fungal strain to different chromium concentrations 100 to 500 ppm was investigated in laboratory scale at different time interval (72, 96 and 120 hrs). Maximum biomass growth and chromium removal rate at pH, 5.0 was investigated, which is continuously increasing with time. Initially 0.04 g of live fungal biomass was added to the waste effluent having different concentration of Chromium (VI) (pH=5, temperature=28ºC, 150 rpm, and glucose as carbon source for fungus). As the Chromium (VI) concentration is increasing in the effluent the biomass growth and chromium removal rate were found as 0.54 g and 99.36% ; 0.34 g and 99.51% ; 0.34 g and 99.38% ; 0.24 g and 99.36% ; and 0.24 g and 99.82% respectively in 100, 200, 300, 400 and 500 ppm respectively at 4 days of incubation. Results indicated that, at 4th day the metal removal reached the maximum level 99.48%. Further incubation did not increase the metal uptake. More than half of Cr (VI) ions were diminished within 72 hrs of contact with live fungal biomass. As we observed from the kinetics (first order kinetics), found that as the Cr6+ concentration is increasing in the effluent the adsorption capacity is decreased simultaneously. As we observe from our result the live fungal biomass is efficient for the removal of fungus.*

Index Terms*: Adsorption, live fungal biomass, kinetics study Freundlich isotherm, Hexavalent chromium.*

Date of Submission: 30-01-2020 Date of Acceptance: 17-02-2020

I. Introduction

1.1 General

Tanning is one of the oldest industry in the world. During ancient time, tanning activity were used to meet there local demands of leather, footwear, drums and musical instrument. With the growth of population, the increase requirement of leather and its product led to establishment of large commercial tanneries. Many years before recorded history people wrapped themselves in dried animal pelts. The problem that the skins turned stiff and rotted was a problem, but ways of softening and preserving the hides were discovered. This was the beginning of leather processing. Initially the hides or skins were probably dried in air and sunlight. Later they may have been soaked in water and dried. Still later it was discovered that certain twigs, barks and leaves soaked with the hides in water helped to preserve them. Through archeologist's findings, it was known that primitive man used the skins of hunted animals for food as well as clothing. Nomadic tribes made shelters from the hides of larger animals, such as bison. As civilization advanced, preserving hides and tanning them into leather became an important industry. In the 18th century tanning was an old and respectable trade and a tedious one. Nearly a year was spent manipulating a hide before it was delivered as leather to the saddle maker, harness maker or other craftsmen.

1.2 Tannery pollutants:

The tanning industry is known to be very polluting especially through effluents high in organic and inorganic dissolved and suspended solids content accompanied by propensities for high oxygen demand and containing potentially toxic metal salt residues. Disagreeable odour emanating from the decomposition of protein solid waste, presence of hydrogen sulphide, ammonia and volatile organic compounds are normally associated with tanning activities (Mohanty, 1997). A significant part of the chemical used in the leather processing is not actually absorbed in the process but is discharged into the environment (Aswathi et al., 2005).

Liquid effluent from light leather processing contains organic matter, chromium, sulphide, and solid waste includes fleshing, wet blue splits, trimmings and shavings, buffing dust etc. The substantial relocation of leather production from the industrialized countries to the developing countries which occurred between the 1960s and the 1980s known as "The Big Shift" in effect moved the most highly polluting part of the process away from the other countries. This occurred under the pressure of increasing cost of labour and cost of effluent treatment installations and operations. This process was accelerated by a combination of restrictions in exports of raw hides and skins and various incentives for higher processing levels provided in developing countries.

Since over 80 per cent of the organic pollution load in terms of BOD comes from early wet processing,

this is the primary target of most pollution control measures. Low waste technologies, generally speaking, require better skilled personnel and closer technical control than conventional processing. Thus, the lack of properly trained staff at different levels remains one of the crucial constraints. The main barriers to the adoption of more environmentally acceptable methods of leather processing and effluent treatment are the additional costs as follows: specialty chemicals required in reducing or eliminating the use of the main polluting chemicals, the cost of purchase and installation of water conservation devices, wastewater collection and reuse equipment; effluent treatment chemicals and process and effluent monitoring equipment; extra personnel and training to maintain technical control of low waste technologies and effluent treatment. Another factor is the traditional conservatism derived from hesitation over process alterations especially when satisfactory leather is being currently produced. This is particularly the case in small to medium scale semi-mechanized family owned units. Another barrier is the frequent remoteness of government-backed R & D facilities from everyday practicalities of leather-making, together with reluctance on the part of traditional tanner groups where resistance to change is compounded by political influence.

The beam-house (un-haring) and the tan-yard require cleaner technologies in leather processing. Also utilization of chrome-free solids as by-products and disposal of chrome containing sludge are possibly the main issues that need particular attention. However, legislation enforcement agencies lack skilled personnel to monitor performance of installed treatment plants. The cost of introducing a cleaner processing method may be prohibitive and beyond reach of a small scale tanner. The price of a special drum for hair save unhairing with the necessary auxiliary equipment may be as much as twice the conventional drum. Enzyme unhairing needs very accurate control and consistency of all parameters (pH, temperature, float, etc) which is possible to achieve only in rather sophisticated tanneries and it is associated with higher production costs (partly off-set by lower wastewater treatment).

1.3 CHROMIUM DISCHARGE IN ENVIRONMENT AND ITS CAUSE

The discharge of Chromium (VI) into aquatic ecosystems has become a matter of concern in all the tannery areas in Bangladesh over the last few decades, (Singh et al., 2009). This pollutant is introduced into the aquatic systems of leather processing units as a result of chrom tanning of leather. Chromium's interactions with biological systems are very different and complex. (Upreti et al., 2004) Toxic kinetics of Cr (VI) show higher rate of penetration into biological membranes as compared to Cr(III). Based on review of available literature, about 10% of ingested Cr(VI) is absorbed in the gastrointestinal tract. The carcinogenicity of Cr (VI) is well documented. Skin ulceration and allergic contact dermatitis have been reported in numerous cases.

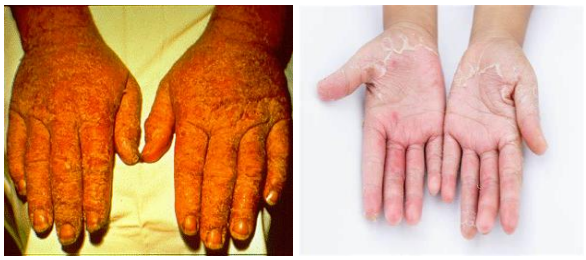

Fig 1.1 Ill effect on human health like skin allegies.

Source: (www. wiakato & mydr.com.au, Distric health board 2010)

Tanneries are typically characterized as pollution intensive industrial complexes which generates widely varying, high strength waste water. Tannery effluent is among one of the hazardous pollutants of industry.

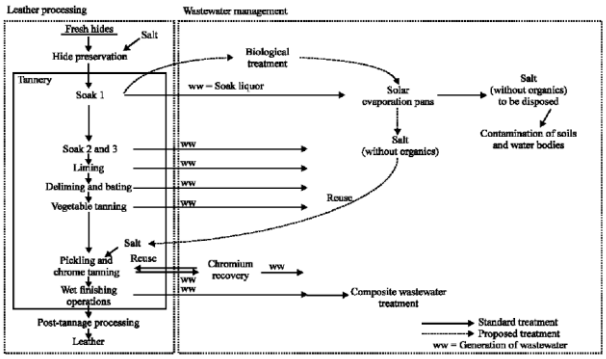

Fig 1.2 Simplified leather production chain and management of the effluent associated.

1.4 TANNERY INDUSTRY IN BANGLADESH:

Recent years have seen a large shift of leather industries from industrialized to developing countries. This has been prompted by both cheaper labour costs and stringent environmental regulations in the former. As the environmental regulations in industrialized countries become stricter, and the cost of compliance increases, leather and many other polluting industries have moved to developing countries.

The conventional leather tanning technology is highly polluting as it produces large amounts of organic and chemical pollutants. These pollutants, which are mostly contained in the effluent discharged by tanneries, are a serious threat to the environment. The tannery effluent, if not treated properly, can cause serious damage to soil and water bodies. The high amount of salt contained in the effluent, for example, can increase soil salinity, reduce fertility and damage farming in large areas. Tanneries also produce harmful gases, dust and a large amount of solid waste. In addition to the large consumption of water and material, tanneries in Bangladesh discharge an estimated 20,000 million liters of effluent per year. The effluent from tanneries is characterized by very high pollutant loads.

Table 1.1 Average Pollution Loads in Tannery Wastewater

Pollution Parameter	Pollution Load in Kg
Biological Oxygen Demand (BOD), 5 days at 20 C	70
Chemical Oxygen Demand (COD)	180
Chlorides as (Cl--)	270
Dissolved solids	600
Suspended Solids	100
Sulphides (as S)	4
Total Chromium	40

Source : Feed Industries Association of Bangladesh (FIAB)

Bangladesh has about 56 tanneries with a total processing capacity of 30,00,000 tons of hides and skins per year. More than 90% of the tanneries are small or medium sized, with processing capacities of less than 2-3 tons of hides/skins per day (Kabdasli et al., 1993). Bangladeshi tanneries process sheep, goatskin, cow and buffalo hides, using both vegetable and chrome tanning. As leather processing requires large amounts of water, most of the tanneries are located near the riverbank. The highest concentration of tanneries in Bangladesh is on the banks of the Buriganga river system in Dhaka.

Table 1.2 Physic-Chemical characteristics of tannery waste

Table 1: Physico-chemical characteristics of tannery wastewater

Reference	pH	TDS	Total solids	Suspended solids	Volatile suspended solids	COD	BOD	TKN	Ammonical/ nitrogen	Chromium	Sulfide
Apaydin *et al.* (2009)	7.4	---	---	2690	1260	3700	1470	---	180	---	440
Ganesh *et al.* (2006)	7.08±0.28	---	10265±1460	2820±140	1505±90	4800±350	---	225±18	128±20	95±55	---
Kongjao *et al.* (2008)	7.0-8.7	18,300 -19,700	---	600-955	---	4100-6700	630-975	144-170	---	11.5- 14.3	---
Koteswari and Ramanibai (2008)	---	15,152	---	2004	1660	8000	930	---	---	11.2	228
Lefebvre *et al.* (2005)	7.70	36,800	---	5800	1300	2200	---	270	---	---	---
Leta *et al.* (2004)	10.72	6810	---	---	---	11163.67	2906	---	162.15	32.87	507.5
Orhon *et al.* (2000)	7.79	---	---	915	578	2155	---	228	168	50.9	35.8
Ram *et al.* (1999)	10.5	17,737	18,884	1147	---	3114	1126	---	33.0	83.00	55.00
Szpyrkowicz *et al.* (2005)	7.7	---	---	---	---	2426	---	370	335	29.3	286
Thanigavel (2004)	8.2-8.5	14750	19775	5025	---	5650	---	---	---	---	---

Except pH all values are in (mg L^{-1})

II. Literature Review

The hides and skins of animals are the source of leather. The skins of large animals such as cattle and horses are referred to as hides. Those of smaller animals such as sheep, goats and calves are called skins. After the hide has been removed it is fleshed, removing any remaining meat tissue or fat. Freshly fleshed hides are shipped in refrigerated trucks to a tannery for immediate processing into leather. If this is not possible, the fleshed hides are cured or preserved by immersion in agitated salty water or brine for 12 hr. After curing, the hides can be stored for several months without rotting and can be shipped to tanneries throughout the world.

The basic raw material for the tannery industry is the raw skin or hide obtained from slaughtered and fallen animals. Raw hides and skins received in tanneries. Prior to talking skin and hides for processing the excess salt has to be removed. The hide and skins are brushed smoothly manually or mechanically to remove as much salt as possible. These hides and skin are subjected to various processes such as soaking, liming, dehairing, fleshing, deliming, and washing.

2.1 TANNERY PROCESSES:

Curing: Deterioration begins immediately when a cow is killed. After the hides are removed from the carcass, they are salted through and through at the slaughterhouses to prevent decay. After they are salted, 55% of the water in the hide is removed, and they are dried for 3 to 6 days. The raw hides are then sold to tanneries.

Soaking: In order for the tanning process to work properly, the dry salted hides must be washed free of the salt. This is done by soaking the hides in water to which chemical wetting agents (similar to household detergents) and disinfectants are usually added for 8 to 20 hours, depending on the thickness of the hides. This soaking procedure rehydrates the hides to their original flaccid condition and removes the dirt.

De-haring: The hair must now be removed from the hides. This is done by soaking the hides in chemicals, or depilatory agents, which destroy the hair by attacking the hair root so it will release freely from the hides, loosen the epidermis, and remove certain soluble skin proteins that lie within the hide substance without destroying the desirable collagen of the hides.

Fleshing: Excess flesh, fat and muscle must now be removed from the hides. This is done with a fleshing machine.

De-liming: All the depilatory chemicals must now be removed from the hides. This is done by washing the hides in ammonium sulfate or ammonium chloride and then clear water in big drums. These chemicals not only clean the depilatory chemicals from the hides, they also adjust the acid-alkaline conditions (pH) to the proper point for receiving the bate, which are enzymes similar to those found in the digestive system of animals. When the bates are applied, they attack and destroy most of the remaining undesirable constituents of the hide.

Pickling: The hides must be placed in an acid environment (low pH) so they will be ready to accept the tanning materials, because chrome tanning agents are not soluble under alkaline conditions. This is accomplished by adding salt and acid to the hides. This is a preserving process in itself, and hides can be kept in this state for extended periods of time without any deterioration.

Tanning: The raw collagen fibers of the hides must be converted into a stable product which is no longer susceptible to rotting. This is done by adding chrome tanning agents to the hides in a revolving drum. These tanning agents also significantly improve the hide's dimensional stability, abrasion resistance, resistance to chemicals and to heat, the ability to flex innumerable times without breaking, and the ability to endure repeated cycles of wetting and drying.

Pressing: The excess moisture must be removed from the hides. This is done by placing each hide through two large rollers similar to those on a clothes wringer.

Shaving: The thickness of the hides must be made uniform all over the hide. This is done with a shaving machine through which the hides are run. The helical shaped cutting blades level the overall thickness to exact specifications and open the fiber structure to better receive subsequent chemical processing.

Secondary-tanning: This process is done to impart special end-use properties with other tanning chemicals. The substances used add solidity and body to chrome leather and help minimize variations in the character of the leather that may still exist between different parts of the hide.

Coloring: As soon as the re tanning process is completed, aniline dyes, derived primarily from petroleum and added to very hot water, are added to rotating drums to penetrate the hides for desired color.

Fat- liquoring: This is the last of the wet chemical operations to which the leather will be subjected. Fat liquoring has the most pronounced effect on how soft leather will be and it contributes greatly to its tensile strength. The more fat liquors that are added, the softer the hides will be.

Staking: Leather is staked to make it pliable. In combination with the correct fat liquoring treatment, staking governs the final firmness or softness of the leather.

Dry Milling: The hides are placed in a large dry drum and tumbled until the desired softness is obtained.

Buffering: This process improves the final appearance of the hides by lightly sanding the surface to remove some of the natural imperfections such as scratches, healed scars, etc. It provides the hide with better cutting yield. In addition to the large consumption of water and material, tanneries in Bangladesh discharge an estimated 20,000 million liters of effluent per year. The effluent from tanneries is characterized by very high pollutant loads.

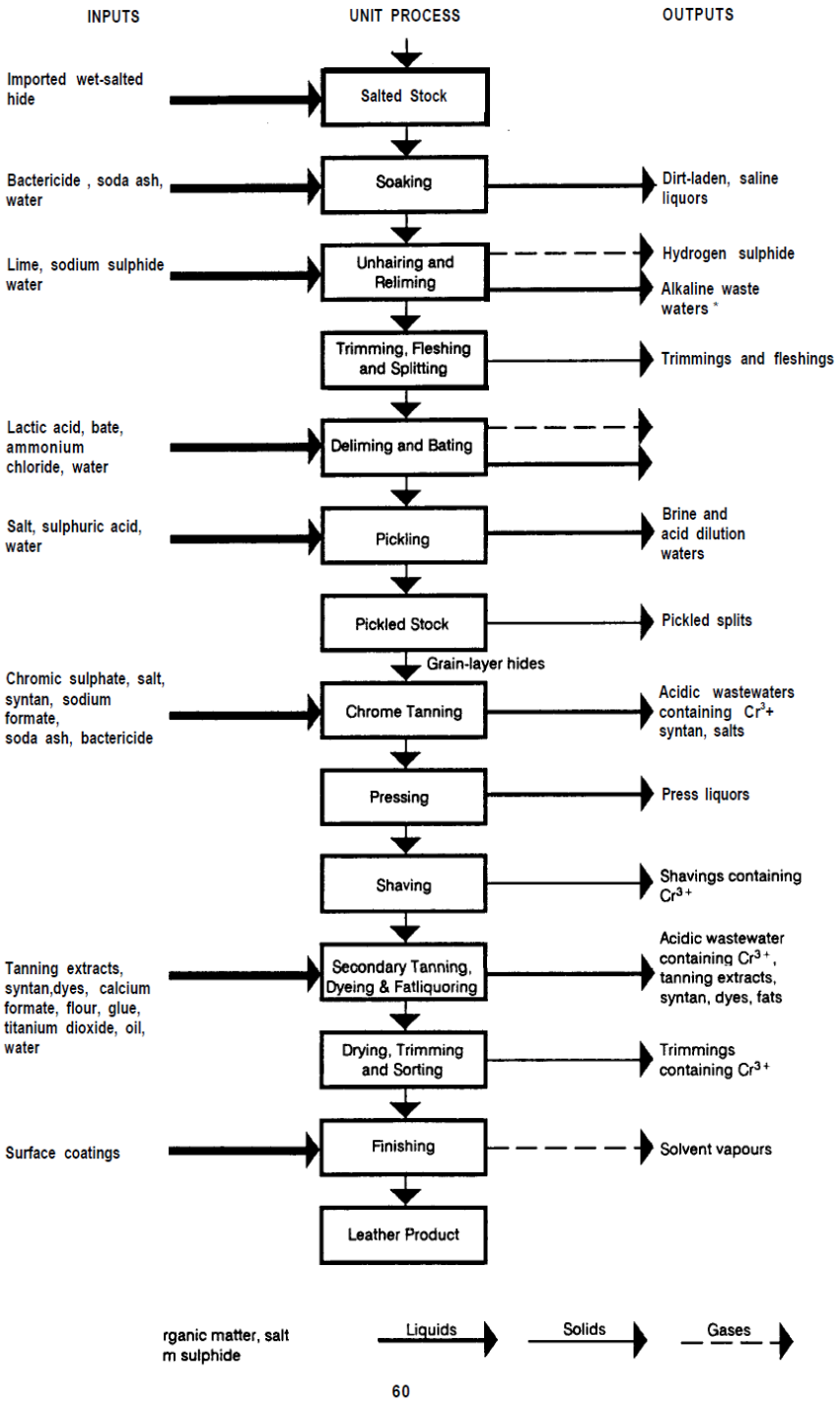

Fig 2.1 Flow diagram of leather making process.

2.2 Cr^{+6} PROBLEM ASSOCIATED FROM TANNERY INDUSTRY:

Tan yard and post tanning operation are responsible for the discharge of chromium. The damage to the environment by the hazardous tannery effluent is becoming an acute problem in the country. The chrome tanning process results in toxic metals, especially chromium (VI) passing to wastewater and are not easily eliminated by ordinary treatment process Tannery wastewaters are mainly characterized by high salinity, high organic loading and specific pollutants such as chromium, Various chemicals used in tanning are lime, sodium

carbonate, sodium bi-carbonate, common salt, sodium sulphate, chrome sulphate, fat liquors, vegetable oils and dyes. The tannery waste water was found to contain higher concentrations of total dissolved solids, chromium, chloride, ammonia, nitrate and sulphates when the samples were collected from the outlets of the industry. Besides these, chemicals such as zinc chloride, mercuric chloride and formaldehyde are used as disinfectants, sodium chloride in curing and as bleaching powder and sodium fluoride to prevent putrefaction, lime in liming, sodium sulphate, ammonium chloride, borax and hydrochloric acid in deliming, sodium for decreasing and basic or acidic dyes in leather finishing.

Hence, the tannery waste is always characterized by its strong color (reddish dull brown), high BOD, high pH, and high dissolved solids. The other major chemical constituents of the waste from the tanning industry are sulphide and chromium. These chemicals mixed with water are discharged from the tanneries and pollute the ground water permanently and make it unfit for drinking, irrigation and general consumption, (Bernal et al., 2006). Therefore there lies an urgent need to determine the pollution levels in the waste waters from these industries.

In Bangladesh there is worst scenario regarding chromium levels, here we show some places where chromium level is high and enormous people effected with chromium. In Bangladesh district Dhaka, it was found that maximum people was effected with chromium, which is coming through the mining and tannery industry. Number of people affected is reported is 3,900,000 in this area. A nasty heavy metal used for stainless steel production and leather tanning that is carcinogenic if inhaled or ingested. In Dhaka (Hazaribagh), which contains one of the largest open cast chromite ore mines in the world, 60% of the drinking water contains hexavalent chromium at levels more than double international standards. In Bangladesh health group estimated that 84.75% of deaths in the mining areas, where regulations are nonexistent are due to chromite-related diseases. There has been virtually no attempt to clean up the contamination.

The first most populous city in Bangladesh, Dhaka is located on the banks of the river Buriganga and is an important industrial center. The city is famous for its leather products and cotton wears. Unfortunately, because of the heavy industrialization, Dhaka is also famous for its pollution. The number of effected people is reported there is 69, 60, 450. Dhaka went into decline after the

1996s, many industries shut down or left the city, and those that remained like the tanneries acquired a bad reputation because they were so polluting. The Buriganga at Dhaka is dirty and synonymous with pollution receiving wastes from the numerous industries and tanneries in and around the city. Doctors in Dhaka say that traffic policemen are among the most at-risk groups for chronic obstructive pulmonary disease.

2.3 CHROMIUM COMPOUNDS:

Metal compounds are not biodegradable. They can thus be regarded as long term environmental features. Since they can also have accumulative properties, they are the subjects of close attention. Two forms of chrome are associated with the tanning industry, whose properties are often confused.

2.4 Chrome3+ [Trivalent Chromium, (Chrome III)]:

Chromium is mainly found in waste from the chrome tanning process; it occurs as part of the retanning system and is displaced from leathers during retanning and dyeing processes. This chrome is discharged from processes in soluble form; however, when mixed with tannery waste waters from other processes (especially if proteins are present), the reaction is very rapid. Precipitates are formed, mainly protein-chrome, which add to sludge generation. If chrome discharges are excessive, the chromium might remain in the solution. Even in low concentrations, it has a toxic effect upon daphnia, thus disrupting the food chain for fish life and possibly inhibiting photosynthesis.

2.5 Chrome 6+ [Hexavalent Chromium, (Chrome VI)]:

Tannery effluents are unlikely to contain chromium in this form. Dichromates are toxic to fish life since they swiftly penetrate cell walls. They are mainly absorbed through the gills and the effect is accumulative. Analysis is highly specialized. The concentrations normally anticipated are very low and analysis is based on colorimetric measurement at 540 nm. Tan yard and post tanning operation are responsible for the discharge of chromium.

2.6 OTHER METALS:

Other metals which might be discharged from tanneries and whose discharge may be subject to statutory limits include aluminium and zirconium. Depending on the chemical species, these metals have differing toxicities that are also affected by the presence of other organic matter, complexing agents and the pH of the water. Aluminium, in particular, appears to inhibit the growth of green algae and crustaceans are sensitive to low concentrations. Cadmium, sometimes used in yellow pigments, is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms.

2.7 PROBLEM ASSOCIATED WITH HEAVY METALS:

The term heavy metals has generally been used to describe those metals having an atomic number greater than iron or having a density greater than 5 g/ml. Plants require certain elements for their normal growth, which are called essential elements (micro and macro elements). But there are also some elements which are not vital for plant growth. Such elements are called nonessential elements, which include heavy metals which cause toxicity to plants (Abou et al.,2008). The contamination of the environment with heavy metals is a serious problem because of industrial activities and sewage sludge applications have largely contributed to the wide spread of these elements in the terrestrial environment (Anuradha et al., 2005).

The presence of heavy metals in industrial and urban waste water is one of the main causes of water and soil pollution (Edday et al., 2006). Heavy metals are ubiquitous environmental contaminants in an industrialized society. Concern over the possible health and ecosystem effects of heavy metals has been increased in recent years (Guidotti et al., 2008). Tremendous increase in the use of heavy metals over the past decades has inevitability resulted in an increased flux of metallic substances in the environment (Gupta et al., 2010). Some metal ions are cumulative poisons capable of being assimilated and stored in the tissues of organisms causing noticeable adverse physiological effects (Adekunle et al., 2010).

The most commonly occurring metals at the discharge sites are lead, chromium, arsenic, zinc, cadmium, copper, and mercury. Presence of these metals in the water and soil may cause serious threat to human health and ecological systems (Bernard et al., 2008). Ultimately metallic components leach to ground water and lead to contamination due to accumulation and resulted in a series of well documented problems in living things (Bernal et al., 2006). Exposure to heavy metals results in acute and chronic toxicity. The functions of kidney, liver and lungs are mainly affected by these metals (Korkina et al., 2007).

The characteristics of tannery waste water vary considerably from tannery to tannery depending upon the size of tannery, chemicals used from specific process, amount of water used and type of final product in a tannery. Tannery waste water is mainly characterized by measurement of BOD, COD. Suspended solid and total dissolved solids, chromium , sulfides etc.

2.8 RETANNING PROCESS EFFLUENT:

The concentrated effluent discharged from retanning process contains unused basic chromium sulphate, tannin extract and synthetic tanning compounds. The wastewater is greenish in color with a pH of about 3.4 to 3.9. This wastewater has BOD varying from 600-800 mg/l and trivalent chromium varying from 600-900 mg/l.

2.9 COMPOSITE WASTEWATER:

Table 2.1 Typical analysis of effluents from semi tanned to finished unit is given below.

Source of sample	pH	BOD (mg/l)	Oil & greases (mg/l)	Boron (mg/l)	Chlorides (mg/l)	Trivalent chromiu m (mg/l)
Stripping	6.4-6.6	1200-2400	Nil	40-20	400-500	Nil
Semi chromium	3.4-3.8	2000-3000	Nil	2.0-3.0	600-750	600-900
Fat liquoring & dying	3.0-4.0	700-1000	300-400	3.4-4.0	80-100	10-20
composite	5.5-6.0	800-1000	40-80	4.0-5.0	500-600	15-25

The composite wastewater discharged from semi tanned to finishing units is brownish in color and has dischargeable odor. It has an average BOD of 800-1000 mg/l and suspended solids of 700-900 mg/l. The pH varies from 5.5-6.6. It contains oil and grease 40-80mg/l and trivalent chromium of 15-25 mg/l.

2.10 ADSORPTION THEORY:

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption. The substance thus adsorbed on the surface is called the adsorbate and the substance on which it is absorbed is known as adsorbent. The adsorptive or ion exchange mechanisms, process is predominantly metabolism Independent. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent). Note that adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon. A number of mechanisms by which microorganisms tolerate and remove heavy metals have been proposed. Microorganisms modulate metal toxicity by maintaining allow intracellular concentration of toxic metals via

precipitation, adsorption to the cell surface, or accumulation in the pericellular or endocellular regions of the cell. The cell walls of the microbial biomass are mainly composed of polysaccharides, proteins, and lipids, and often contain functional groups such as carboxylate, hydroxyl, sulphate, phosphate, and amino groups that bind to heavy metals. Carboxylic acid and phosphate groups have been reported to take part in metal binding by brown algae. Proteins have been implicated in the binding of metals to phytoflagellates. Fourest and Volesky have studied the involvement sulfonate groups and alginate in biosorption by a dry biomass of Sargassum fluitans. The mode of interaction between metal species and microbial cell components may be simple adsorption, ion exchange, electrostatic interaction, complexation, precipitation, and crystallization. Endocellular accumulation (bioaccumulation) of metals involves metabolism-dependant uptake and storage in intracellular organelles such as vacuoles, or binding to cysteine-rich small proteins such as metallothioneins. Microorganisms are also capable of transforming metals from one oxidation state to another.

Hexavalent chromium Chromium (VI), which is toxic to most biological systems, is generated in variable amounts by leather tanning and electroplating processes. The kinetics of this kind has been studied with the help of freundlich isotherm.

Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. The two isotherms depend on temperature and they have two constants each in their general form. Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption. The Freundlich constant, n also indicates the degree of favorability of adsorption (Treybal et al., 1981). Both the isotherms depend upon temperature. Highly alkaline pH (pH 8–10) was least favorable for Cr adsorption to biomass and such conditions enhanced the weakening of adsorption forces and thus facilitated elution of bound Cr ions and its release into the aqueous system.

The Freundlich isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad \text{……. (1)}$$

Where KF is a rough indicator of the adsorption capacity and 1/n is the adsorption intensity. In general, as the KF value increases the adsorption capacity of an adsorbent for a given adsorbate increases. Eq. (1) may be linearised by taking logarithms. The high magnitude of 'KF' and 'n' illustrate high adsorption capacity of free biomass over immobilized forms.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Conformation of the experimental data into Freundlich isotherm indicates the heterogeneous nature of the fungal surface.

Nouri et al. in 2005 studied and recognized the capability of algae, fungi, and bacteria in the removal of heavy metals from industrial effluent. In this research, growth of Aspergillus oryzae in the tanning house effluent, and its capability in chromium bio removal were assessed. Aspergillus oryzae can grow in different concentration of Chromium (VI), 120-1080 mg/L. Maximum biomass growth and chromium removal rate at pH, 3.3, Chromium (III) concentration equal to 240 mg/L and inoculum size equal to 0.12% (dry weight) were 0.25% (dry weight) and 94.2%, respectively. Effects of various factors such as pH, temperature, shaking velocity and nutrients were also investigated. At optimum conditions (ie: pH=5; temperature=30ºC, shaking velocity=150 rpm, and nitrogen source of dihydrogen ammonium phosphate concentration=0.3%), biomass growth and chromium removal rate were found as 0.45% of dry weight and 99.8%, respectively. Effect of detention time showed that after 30h, biomass growth and chromium removal rate were 0.28% and 97.6%, respectively. Statistical studies on factors such as pH, temperature, shaking velocity, type and concentration of nutrients on the "biomass growth" and "residual chromium", showed that all of the factors had significant effects ($\alpha = 0.05$, $P < 0.001$). Therefore A.niger capable grow in the tannery industries effluent with 240 mg/L chromium and 97.6% chromium removal rate.

Yeoung et al in 2004 have done the work on removal of hexavalent chromium from aqueous solution was carried out in batch experiments using dead biomass of four fungal strains Aspergillus niger, (Srivastava et al., 2006). Rhizopus oryzae, Saccharomyces cerevisiae and Penicillium chrysogenum. All of these dead fungal biomass completely removed Cr(VI) from aqueous solutions, that of R. oryzae being the most effective. Cr(VI) was removed from aqueous solutions by the reduction to Cr(III) when it contacted with the biomass. The removal rate of Cr(VI) increased with a decrease in pH or with increases of Cr(VI) and biomass concentrations. In particular, the removal rate of Cr(VI) was proportional to total chromate concentration [Cr(VI)], and equivalent concentration of organic compounds. To screen the efficient biomass for Cr(VI) removal, the time-dependent concentration of Cr(VI) was measured in a batch system containing three species of mould (A. niger, R. oryzae and P. chrysogenum) and one species of yeast (S. cerevisiae) , the initial removal rate of Cr(VI) depended on species of fungi, the order was R. oryzae > S. cerevisiae > P. chrysogenum > A.

niger. In all of the fungal species studied, Cr(VI) sharply decreased and it finally disappeared inaqueous solution. R. oryzae completely removed Cr(VI) in 48 h, while others needed 218–254 h for the complete removal of Cr(VI). Although initial removal rate of Cr(VI) by S. cerevisiae was faster than that by A. niger, the former required more contact time than the latter to completely remove Cr(VI) from aqueous solution. Interestingly, R. oryzae showed the poorest removal efficiency of total chromium. The removal efficiency of total chromium decreased in the order S. cerevisiae > P. chrysogenum > A. niger > R. oryzae. The difference between total Cr and Cr(VI) concentrations in aqueous solution indicates the generation of Cr(III) due to the reduction of Cr(VI). Thus, it may be mentioned that Cr(VI) could be reduced to Cr(III) by any fungal biomass including A. niger, the removal capacity of Cr(VI) for 24 h of contact time decreased in the order R. nigricans > R. arrhizus > A. oryzae > A. niger. These results lead us to the conclusion that the Rhizopus species is most efficient fungal biomass for Cr(VI) removal. However, it was difficult to correlate the Cr(VI) removal capacity of each fungal biomass with structural and/or functional characteristic(s) of it, i.e., each species of fungi differs in the cell wall structures and cell components, resulting in different Cr(VI) reducing capacity and adsorption capacity. Therefore, a further, fruitful direction of this study would be to examine the role of structural and functional characteristics of fugal biomass on Cr(VI) reduction. The contact time required for the complete removal of Cr(VI) varied from 17 to 170 h depending on the solution pH. These results were due to the depletion of the protons participating in the reduction of Cr(VI). The concentration of Cr(VI) versus time was examined at various initial Cr(VI) concentrations in the range of 25– 200 mg/l The removal rate of Cr(VI) increased with an increase in initial Cr(VI) concentration. In conclusion, as an alternative to much more expensive reagents and systems, the abundant and inexpensive dead fungal biomass may be used for the conversion of toxic Cr(VI) into less toxic or nontoxic Cr(III).

Vankar et al in 2007 used phyto-remediation technique for the treatment of tannery effluent. The tannery effluent carrying hazardous Cr(VI) species due to the oxidation of Cr(III) species was found to pollute the soil and the ground water of Hazaribagh area of Dhaka city where a large number of tanneries are located. We have studied the phyto-remediation of Cr(VI). Biosorption of the chromium ion Cr(VI) onto the cell surface of Trichoderma Urbina. Fungal species in aerobic condition was investigated. Batch experiments were conducted with various initial concentrations of chromium ions to obtain the sorption capacity and isotherms. The results obtained at pH 5.5 of chromium solution were 97.39% reduction by non pathogenic species of Trichoderma. It was found that the sorption isotherms of fungi for Cr(VI) appeared to fit Freundlich models. The results of FT-IR analysis suggested that the chromium binding sites on the fungal cell surface were most likely carboxyl and amine groups. The fungal surfaces showed efficient biosorption for Chromium in Cr(VI) oxidation state (Yousefi et al., 2009). Best results for sorption were obtained at 5.5–5.8 pH, at low or high pH values, Cr(VI) uptake was significantly reduced. The study of biosorption showed significant chromium uptake by Trichoderma filamentous fungi almost 100% by this non pathogenic species i.e., 10 ppm on wet weight of the fungi. Since metal biosorption from solution was predominantly due to physico/chemical interactions between the biomass and metal in solution, morphological differences existing within biomass can greatly influence the biosorption process. The cellular structure of Trichoderma mainly contains polysaccharide which can make significant difference in metal uptake by this species. Thus this fungal species can be a good source of cost effective biosorbent through biotechnological development for removal of Cr(VI) from industrial effluents in a potential manner. Another very important aspect of this study is the future use of the fungal strain in biosorption of other heavy metal species coexisting in various industrial effluents.

Saumic et al in 2010 used live fungal biomass for removal of Cr (VI). Response of Trichoderma harzianum strain to different chromium concentrations was investigated by poison food technique. It was noticed that, the mycelial growth was inhibited up to 94 % at 40 mg/l concentration followed by30mg/l (91%).The chromium (VI) biosorption ability of Trichoderma harzianum was tested in-vitro. The organism was inoculated on Czapek Dox broth medium containing 30 mg/l of Cr (VI) salt. The metal residues were analyzed at different day's interval (4, 5, 6 and 7 days). The effect of different pH and temperature on metal removal was also investigated. Results indicated that, at 7th day the metal removal reached the maximum level (90.2%). Further incubation did not increase the metal uptake. A pH range of 4-5 and temperature of 30 °C was optimum for Cr (VI) removal by T.harzianum in the present study. In the present study, it was observed that the selected Trichoderma harzianum strain was able to remove hexavalent chromium from the aqueous solution. Though there was not much reports was available on the role of Trichoderma harzianum with biosorption capability, the present study had indicated that this fungal strain can also be used as a material for effective removal of heavy metal from aqueous solutions.

Deng et al in 2008 used dead green algae for the removal of Cr (VI) .Biosorption of Cr(VI) from aqueous solutions by nonliving green algae Cladophora albida was investigated in batch experiments. The influence of pH, algal dosage, initial Cr(VI) concentration, temperature and coexisting anions on removal efficiencies of C. albida was studied. Cr(VI) removal process was influenced significantly by the variation of pH, and the optimum pH was chosen at a range of 1.0–3.0. The optimum algal dosage 2 g/l was used in the experiment. The removal rate of Cr(VI) was relatively rapid in the first 60 min, but then the rate decreased

gradually. Removal mechanism was studied by analyzing Cr(VI) and total Cr in the solution. Biosorption and bioreduction were involved in the Cr(VI) removal. Biosorption of Cr(VI) was the first step, followed by Cr(VI) bio reduction and Cr(III) biosorption on the algal biomass. Actual industrial wastewater was used to evaluate the practicality of the biomass C. albida. From a practical viewpoint, the abundant and economic biomass C. albida could be used for removal of Cr(VI) from wastewater by the reduction of toxic Cr(VI) to less toxic Cr(III). Biosorption properties of C. albida were studied as a function of pH, initial Cr(VI) concentration and temperature. The removal of Cr(VI) increased with the increasing temperature and decreasing pH at the same initial concentration of Cr(VI), and increased as the increasing initial concentration at the same pH and temperature. The removal rate of Cr(VI) was relatively rapid in the first 60 min, but then the rate decreased gradually. The mechanism of Cr(VI) removed by C. albida was is not "anionic adsorption" but "adsorption coupled reduction". Cr(VI) adsorbed on the biomass is reduced to Cr(III) and released to solution gradually. Actual industrial wastewater was used to evaluate the practicality of C. albida. The results showed that C. albida was an effective and economical biosorbent material for removal of Cr(VI) from wastewater. However, further research is needed to establish the process with specific attention to the regeneration of the sorbent and the recovery of the sorbed metal. Therefore, future research will be oriented towards column studies.

Sen et al in 2010 isolate fungus from soil and used for the removal of Cr(VI) from aqueous solution using biological sources as biosorbent has assumed advantageous over the existing conventional physico-chemical techniques for the treatment of metal contaminated wastes. The present batch biosorption study was undertaken with an aim to examine the Cr (VI) removal potential of the resting cells of Fusarium solani (isolated from soil) from aqueous solution. The specific Cr (VI) removal decreased with increase in pH and increased with increase in initial Cr(VI) concentration , up to 500 mg/l . The specific Cr(VI) removal remained almost constant by increasing biomass concentration from 2.4 to 5.2 g/l. The studies also carried out by using the resting cells obtained from various stages of growth and the maximum specific Cr(VI) removal (60 mg/g) was achieved at 500 mg/l initial Cr(VI) concentration and by using cells (36 h old). The Langmuir adsorption isotherm constants, Q0 and b were observed to be 57.1 mg/l and 0.06 l 1/mg, respectively. The resting cells of the Fusarium solani used in the present study was found

to be not only tolerant to very high concentrations of Cr(VI) but also effective in Cr(VI) removal. Cr(VI) removal potential of resting cells of the Fusarium solani is compared with the potential of resting cells of different organisms reported in the literature. Most of the studies reported with resting cells of different bacteria and fungi carried out at lower initial Cr(VI) ion concentrations, clearly indicates lower tolerance of the organisms for Cr(VI). In most of the cases the maximum tolerance limit was found to be 50 mg/l beyond which the growth as well as the Cr(VI) removal were inhibited. In the present study, Fusarium solani was found to be tolerant even upto 1000 mg/l Cr(VI) concentration.

Juan et al 2010 used fungal strain which is resistant to Cr (VI) and capable of removing the oxyanion from the medium was isolated from the environment near Chemical Science Faculty, located in the city of San Luis Potosí, Mexico. The strain was identified as Paecilomyces sp, by macro and microscopic characteristics. It was concluded that application of this biomass on the removal of Cr (VI) in aqueous solutions can be used since 1 g of fungal biomass remove 100 and 1000 mg/100 ml of this metal after one and three hours of incubation, and remove 297 mg Cr (VI) of waste soil contaminated, and this strain showed the capacity at complete concentrations reduction of 50 mg/l Cr (VI) in the growth medium after 7 days of incubation, at 28°C, pH 4.0, 100 rpm and a inoculum of 38 mg of dry weight. These results suggest the potential applicability of Paecilomyces sp for the remediation of Cr (VI) from polluted soils in the Fields. The ability of some microorganisms for interact with different Cr forms makes them attractive in the context of environmental biotechnology. In this sense, the use of microbial biomass for the removal of Cr from industrial wastewater and polluted water has already been recognized. The properties of some microorganisms for both: tolerate and reduce Cr (VI) enable their application in biotechnological process focusing on detoxification of Cr (VI). Cr resistance has been described in bacteria and fungi isolated from Cr-polluted environments. Yeast strains isolated include Candida and Rhodosporidium genera, but in these, the general mechanism of chromate resistance is related to limited ion uptake, rather than to chemical reduction of the toxic species (Baldi et al.,1990; Pepi et al., 1992). However, other yeasts such as Candida utilis (Muter et al., 2001) and Candida maltose (Ramírez et al., 2004), showed partial ability to reduce Cr (VI) and also the capability to accumulate Cr in the biomass. Recent reports have also examined Cr (III) and Cr (VI) uptake and accumulation by different filamentous fungi (Acevedo et al., 2008; Fukuda et al., 2008; Srivastava et al., 2007; Morales., 2008). The present study report the isolation and identification of a Paecilomyces sp fungal strain that exhibits high resistance level, resistance, biosorption and reduction potential to Cr (VI).

Morales et al in 2007 used fungal strain for removing hexavalent chromium was to be isolated from industrial effluent from a leather factory located in the city of Guadalajara, state of Jalisco, Mexico. The strain was identified as Trichoderma inhamatum by the D1/D2 domain sequence of the 28S rDNA gene.Batch cultures of T. inhamatum in media containing initial Cr(VI) concentrations from 0.83 to 2.43 mM Cr (VI) were prepared.

Experimental results suggest that the fungus is capable of transforming hexavalent chromium to trivalent chromium; a transformation of a highly toxic contaminant to a low toxic form. The specific and volumetric rates of Cr(VI) reduction by T. inhamatum cultures decreased as the initial Cr(VI) concentration increased. The fungus exhibited a remarkable capacity to tolerate and completely reduce Cr(VI) concentrations up to 2.43 mM. These results indicate that the T. inhamatum fungal strain may have potential applications in bioremediation of Cr(VI)- contaminated wastewaters. The T. inhamatum fungal strain was isolated from tannery wastes by enrichment culture techniques. The strain showed capacity to completely reduce concentrations of Cr(VI) up to 2.43 mM under aerobic conditions. Cr(VI) reduction characteristics exhibited by T. inhamatum suggest that this fungus could be useful for the bioremediation of Cr(VI)-laden wastewaters.

Prasenjit et al in 2005 used Aspergillus foetidus which has the ability to take up chromium during the stationary phase of growth and under growth-non supportive conditions. We observed a 97% decrease in hexavalent chromium (initial concentration 5mg/g) at the end of 92 hr of growth, which may be due to its reduction to Cr (III) and/or complexation with organic compounds released due to the metabolic activity of the fungus. Replacement culture studies under growth-non supportive conditions revealed that the maximum uptake of Cr (VI) at pH 7.0 is 2 mg/g of dry biomass. At low or high pH values, Cr (VI) uptake is significantly reduced. In addition, the initial rate of total chromium uptake is also enhanced by higher biomass concentrations and the presence of glucose. The results obtained through this investigation indicate the possibility of treating waste effluents containing hexavalent chromium using Aspergillus foetidus. The fungal isolate Aspergillus foetidus is effective in their removal of chromium. Although these results suggest the possibility of treating waste effluents using this fungus, further experiments need to be carried out with the objective of optimizing the conditions which would allow a more efficient metal removal from wastewater, and biosorption/ biotransformation of metal ions from a technical and economic point of view.

III. Materials And Methods

All the chemicals used and reagents employed were of analytical grade with sufficient purity. The calibration curves were prepared prior to estimation of unknown concentration and used throughout the study.

3.1 COLLECTION OF SAMPLE

EFFLUENT SAMPLE

The effluent were collected from tannery industry situated in Hazaribagh and it was stored in refrigerator at 4^0C until further investigation was carried out.

3.2 CHROMIUM (VI) ESTIMATION BY SPECTROPHOTOMETER:

Determination of total Chromium 100ml was digested with H_2SO_4 –HNO_3 digestion method (3030G), diphenylcarbazide method worked out for Chromium estimation (3050-Cr D of slandered method).

3.3 ADSORPTION STUDIES:

Effect of Chromium (VI) concentration was studied in tannery effluent, through tannery effluent have 0.45 mg/l Chromium (VI). We added 100 mg/l to 500 mg/l of additional chromium to check the efficiency of fungal isolates. The initial pH of the effluent was adjusted 5 with .1N HCl. The chromium solution 100 to 200 mg/l was added in different flask with effluent and 1gm /100ml glucose as a carbon source. Sterilize the effluent at 121 o C, 15 psi for 10 min. The 0.04 gm of live fungal cell which is having 5mm of diameter was inoculated in 50 ml of effluent, the Chromium (VI) adsorption was checked from 0 hr to 120 hr. We added $K_2Cr_2O_7$ in our effluent.

3.4 ISOLATION OF FUNGUS

Fungus is isolated from tannery sludge itself. 1 gm sludge sample was added in the potato dextrose broth and incubated for 3 days at 28 ^{0}C on shaker at 120rpm. Fungus isolates from the sludge samples were identified on dehydrated medium. The different fungus on the basis of color(pigment product) spread on agar plate. The isolate culture preserved at 4 ^{0}C after growing on PDA slant.

3.5 MORPHOLOGICAL CHARACTERISTICS

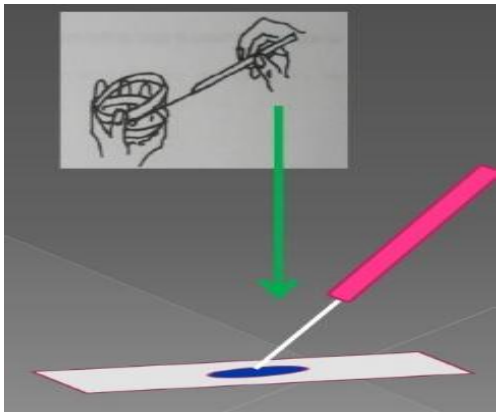

Fig 3.1 Morphological characteristics

3.5.1 PROCEDURE:

Using an inoculating needle, pick a small portion of small fungus growth and place on separate slide containing a drop of lactophenol-cotton blue. Put a cover slip, examine under low and high power objectives. Observe characteristics arrangement, size, shape, nature of growth (fluffy, velvety, powdery, dry, moist) and color of growth on surface and reverse side.

3.6 CHARACTERISTICS OF EFFLUENT:

Characterization of effluent was done according to the method given in APHA (2005).

Biological Oxygen Demand:

Biochemical Oxygen Demand (BOD) refers to the amount of oxygen that would be consumed if all the organics in one liter of water were oxidized by bacteria and protozoa.

It was estimated by the method 5210 B (APHA).

TSS, TDS and Total Solids:

Solids were dried at 105^0C till constant weight according to the method no. given 2540 B, 2540 C, 2540 D respectively for TS, TDS and TSS. (APHA)

Chemical Oxygen Demand:

The Chemical Oxygen Demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. It was estimated by the method no. 5220 C closed refluxed titration method. (APHA)

Chloride Test:

In a neutral or slightly alkaline solution Potassium Chromate can indicate the end point of the Silver Nitrate titration of Chloride. The method no. used was 4500-Cl- B.

The characteristics of water samples such as pH, COD, BOD, TSS,TDS, TS and chloride were determined using standard methods of APHA.

IV. Result And Discussion

4.1 CHARACTERIZATION OF TANNERY EFFLUENT

Table 4.1 characteristics of tannery effluent

Parameter	Value
pH	11.5
COD	3800
BOD	2000
TS	12000
TDS	9500
TSS	4500
Chloride	550
Cr^{+6}	0.44

ALL values, except pH , are in mg /l.

The effluent of tannery industry which has a pH value around 11.5. The waste water from the industry is very polluting. The amount of oxygen needed to consume the organic and inorganic materials is called the Chemical Oxygen Demand (COD). It has been found that their Chemical oxygen demand can be around 3800 mg/L. Biochemical Oxygen Demand (BOD) refers to the amount of oxygen that would be consumed if all the organics in one liter of water were oxidized by microorganisms. The BOD value is calculated and its value comes 2000 mg/L. Total solids is a measure of all the suspended, colloidal, and dissolved solids in a sample of

water and its value in the effluent is estimated as 12000 mg/L. Total Dissolved Solids is 9500 mg/l a measure of the combined content of all inorganic and organic substances contained in a liquid and total suspended solid is 4500mg/l. Chloride concentration in this waste water effluent is found to be 550 mg/L.

4.2 ISOLATION OF FUNGUS

Fungus is isolated from tannery sludge itself. 1 gm sludge sample was added in the potato dextrose broth and incubated for 3 days at 28 ^{0}C at 150 rpm. Fungus isolates from the sludge samples were identified on potato dextrose agar plates and further fungal strain is maintained on the PDA plates at 4 ^{0}C.

4.2.1 SCREENING OF FUNGAL STRAIN:

A total of 4 fungal strains were isolates were screened for their growth on PDA from tannery sludge sample, all the 4 isolates were used for chromium removal efficiency at 100 ppm, one fungal strain A was best suited for chromium removal efficiency on PDA. Then isolate A was further used for adsorption of chromium (VI) on effluent from 100- 500 ppm chromium (VI).

4.2.2 IDENTIFICATION OF SELECTED FUNGAL ISOLATES

4.2.2.1 MORPHOLOGY OF FUNGUS:

Total 4 fungal strains isolates isolate were screened for their growth, Out 4 fungal strain, one fungal strain (A) ,were best suited for chromium removal efficiency of the effluent. The fungal morphology is white, toff , feathery, fluffy and usually spreading in nature. Its surface white in centre with yellow circle on it.

Fig 4.1 Fungal Culture

4.3 STUDIES WITH LIVE FUNGAL BIOMASS:

4.3.1 EFFECT OF CR (VI) CONCENTRATION:

4.3.1.1 ADSORPTION KINETICS:

Different concentration of Chromium (VI) (100-500ppm) was used to check their adsorption by live fungal.

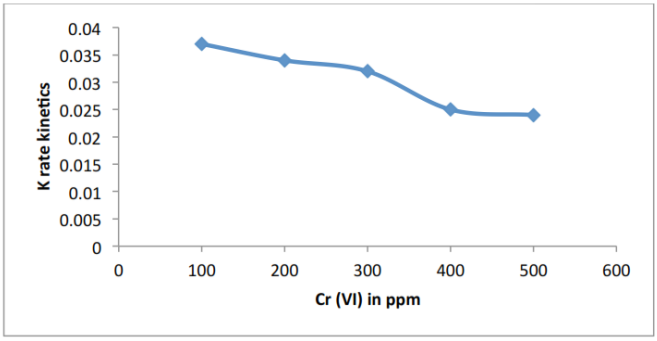

Fig 4.2 Rate of removal of Chromium (VI) at different concentration at 120hr.

4.4 RATE KINETICS:

This was may be due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the lack of binding sites for the complexation of Chromium (VI) ions at higher concentration levels. At lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitated 99.36% adsorption in 120 hr. At higher concentrations, more Cr ions are left unabsorbed in solution due to the saturation of binding sites (Ahalya et al., 2005). We observed from the fig. 4.2, rate kinetics is been decreasing continuously. As we observed from the fig. 4.2, it shows the first order kinetics.

$$\log(qe - q) = \log(qe) - Kadt /2.303$$

where qe and q (both in mg/g) are the amount of Chromium adsorbed per unit mass of a live fungal biomass at equilibrium and time t, respectively, and K*ad* (adsorption rate constant) is the rate constant (min−1).

4.5 REMOVAL OF CR (VI) IN INDUSTRIAL WASTES WITH FUNGAL BIOMASS

Live fungal bid was added (wt is .04g) for eliminating Cr (VI) from industrial wastes, the mycelium biomass was incubated with contaminated effluent having different concentration of Chromium (VI) (100 to 500 ppm), pH 5.0. It was observed that after 120hr of incubation with the fungal biomass, the Cr (VI) concentration of effluent sample decrease fully. The decrease in Cr (VI) levels occurred at a different rate, at 72 hr of incubation are of 75.0%, 71.0%, 70%, 46%, and 45% in 100 to 500 ppm respectively. We added additional $K_2Cr_2O_7$ in our effluent.

Table 4.2 Uptake of Chromium (VI) at different concentration.

Uptake rate (q_e) of chromium (VI)					
Time(hr)	100ppm	200 ppm	300 ppm	400 ppm	500 ppm
72	805.0	997.6	700.0	1852.6	2035
84	662.0	665.9	728.0	2869.6	3189.5
96	289.5	277.1	694.3	2429.5	2897
108	256.5	254.3	265.4	1520.0	1540.0
120	110.5	178.3	188.5	778.3	1042.9

qe value is in (mg Cr(VI)/g)

4.6 EFFECT OF BIOMASS ON ADSORPTION

The removal of 100ppm to 500ppm of Cr (VI) with fungal biomass at 28°C, were studied because the maximum percentage of metal is removed at 72 hr to 84 hr by using different fungal biomass which is continuously growing in the flask. The fungus takes more time to grow comparatively to bacteria. It was observed from the result that as the amount of biomass, increased with time the removal of Cr(VI) in solution was also increased. As the concentration of chromium was increased the metal biosorption site, was unavailable for the binding of metal on the surface of fungal mycellium. It was observed from the fig. 4.3 to 4.7 that at different biomass which is growing with different concentration of chromium showed different growth pattern.

The fig 4.3, biomass is increasing with the time (time is taken from 0 hr to 120 hr) chromium (VI) is removed 99.36% with 100 ppm Chromium (VI) concentration in 120hr. The biomass from 0 to 72 hr is also negligible (0.065 g). After 72 hr the growth of the biomass started increasing and continue up till 120 hr but maximum chromium(VI) was adsorbed within 72 hr which is 75.0%. After 72 hr experiment was further extend to the 120 hr and observed 99.36%, chromium(VI) was adsorbed in 120 hr. It indicated that as the contact time is increased adsorption was also increased but after 84 hr the adsorption rate is marginal. As we observed from table 4.2, the maximum.

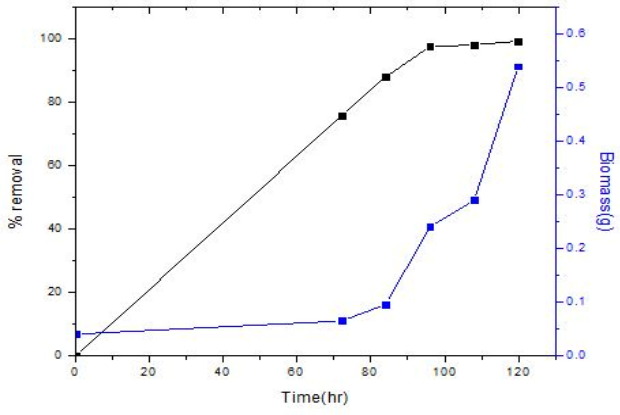

Fig 4.3 Effect of biomass on removal of Chromium (VI) at 100ppm with respect of time.

uptake of Chromium (VI) was 805 mg/g, which is reported at 72 hr. In 84 hr it was 662.0 mg/g, but after reaching from 96 to 120 hr, the drastic decrease in uptake rate was observed which was supported by Ahalya et al (2005).

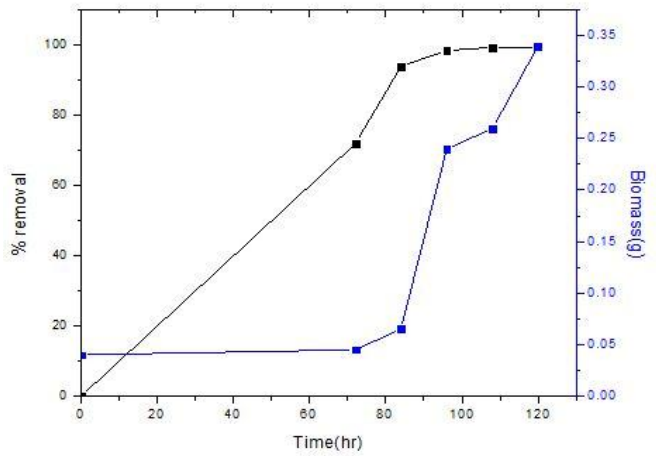

Fig 4.4 Effect of biomass on removal of Chromium (VI) at 200ppm with respect of time.

Biomass in 200 ppm was also increased with the time (0 hr to 120 hr) chromium (VI) was removed 71% with 200ppm. Fig. 4.4, showed that the growth of fungus started after 72 hr and as soon as biomass was increased and consequently the removal efficiency was also increased, and after 120 hr of incubation 99.51% of Chromium (VI) had been removed from the effluent (biomass is 0.34g), but as observed from the results in Fig. 4.4, after 84 hr the adsorption rate is marginal. The increase in biomass is suddenly shoot up from 0.065 g to 0.24 g and adsorption rate is also increased from 71% to 99.36%. The uptake rate of Chromium (VI) also supported the results. The maximum uptake rate was in 72 hr which is 951.72 mg/g and in 84 hr it was 658.88 mg/l , which is again decreased in 96 to 120 hr, which ranges from 256.06 to 198.33 mg/l.

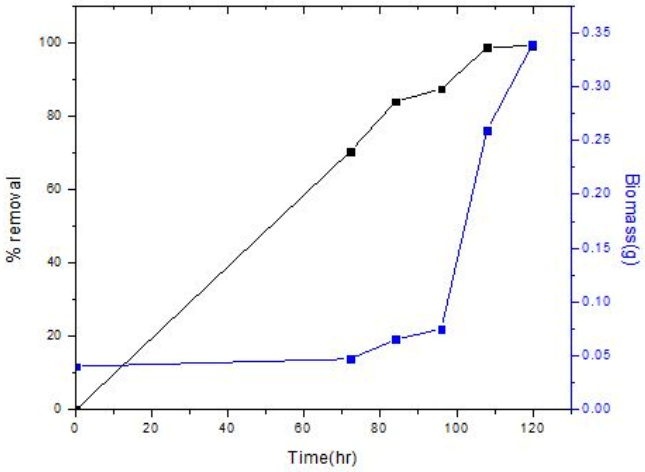

Fig 4.5 Effect of biomass on removal of Chromium (VI) at 300ppm with respect of time.

In 300 ppm metal concentration was increased with time (0 hr to 120 hr) and chromium (VI) was removed 70.37% in 72 hr. It was observed some fluctuation between 72hr to 96 hr, it stated that maximum removal was observed in that period. chromium (VI) concentration. Fig. 4.5, showed that the growth of fungus started after 72 hr and as soon as biomass is increasing the removal efficiency was also increased after 96 hr the biomass suddenly shoot up from 0.06 to 0.25 g and fluctuation was also be their in 72 to 96 hr. But after 96 hr the adsorption rate was found marginal. After 120 hr of incubation 99.38% of Chromium(VI) was removed from the effluent (biomass is 0.34g) In 72 hr, it was found 600 mg/g which indicate fungus has taken some time for their growth due to availability of more substrate. In case of 96 hr the uptake rate near to 84 hr but after 108 hr to 120 hr the uptake rate decreased drastically as shown as table 4.2.

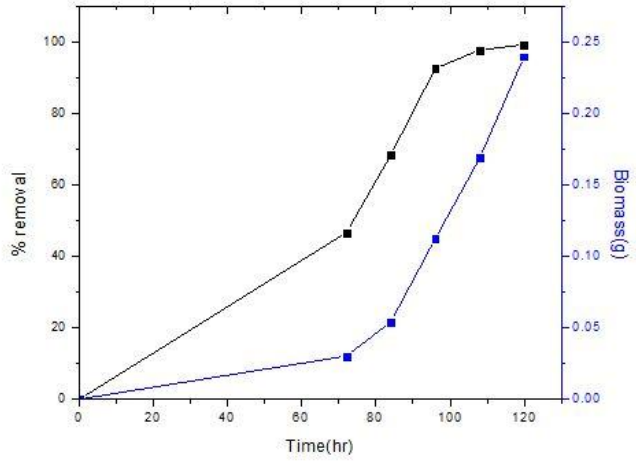

Fig 4.6 Effect of biomass on removal of Chromium (VI) at 400ppm with respect of time

From figure 4.6 biomass was increased with the time (0 hr to 120 hr), adsorption is relatively decreased initially, which is observed 46.70% and slightly increasing with time at 84 hr which is reported 68.38% which indicated that the toxicity level is suppressing the biomass growth and it effect the adsorption phenomena ultimately and also may be due to high concentration of chromium (VI) the fungus took much time for adsorption in this atmosphere. After the 120 hr of incubation, 99.36%, chromium (VI) is been removed from the effluent (biomass was 0.24g). Fig. 4.6, showed that the growth of fungus started after 72 hr and as soon as biomass was increased the removal efficiency was also increased, but after 84 hr the adsorption rate is marginal. The adsorption phenomenon was supported by uptake rate of chromium (VI) by fungal biomass. Table 4.2 showed maximum uptake rate was 2862.67 mg/g Chromium (VI) in 84 hours and in 96 hours 2328.65 mg/g which was more than 1752.66 mg/g in 72 hours. The Chromium (VI) also followed the same pattern as in figure 4.6. So it was concluded from the graph if biomass would have increased uptake rate also increased.

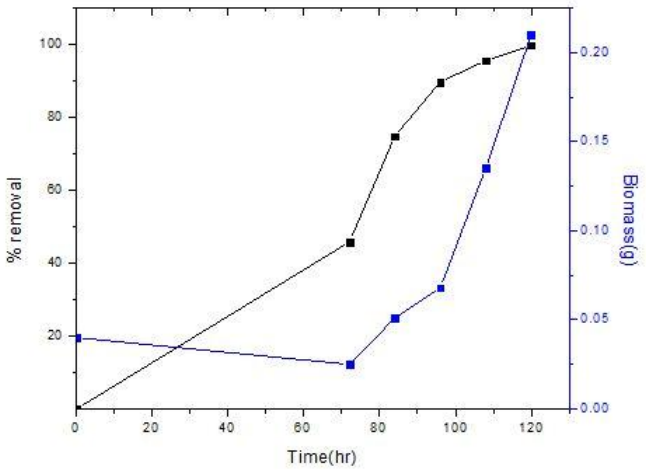

Fig 4.7 Effect of biomass on removal of Cr^{6+} (500ppm) with respect of time

The similar type of results were found in 500 ppm concentration of Chromium (VI). Biomass was increased with the time (0 hr to 120 hr) but as observed from the fig. 4.7 the adsorption was relatively decreased initially, which was observed 45.86% and slightly increasing with time at 84 hr which was reported 74.76% respectively, it indicated that the toxicity level was suppressing the biomass growth and it affected the adsorption phenomena ultimately. After the 120 hr of incubation, 99.82%, chromium(VI) had been removed from the effluent (biomass was 0.21g). Fig. 4.7, showed that the growth of fungus started after 72 hr and as soon as biomass was increasing the removal efficiency was also increased, but it was observed from table 4.2, the maximum uptake of Chromium(VI) was 3185.45 mg/g, which was reported at 84 hr and 2867 mg/g Chromium (VI) in 96 hrs which was more than 2034 in 72 hr. These results indicate that once fungal biomass adopt the Chromium (VI) the biomass increase steeply and Chromium (VI) uptake rate (qe) is also increased.

4.7 EFFECT OF CONTACT TIME AND REMOVAL MECHANISM

The influence on removal efficiency was significant by varying the contact time. As shown in Figs.4.3 to 4.7, it could be seen that removal process was consisted of three phases:

1. Primary rapid phase.
2. Second slower phase.
3. Slowest phase

The primary rapid phase accounted for almost the half part in the total metal adsorption and lasted approximately 84 hr. This is because the kinetics of metal adsorption, which depends on the physical sorption on the cell surface, is usually rapid during the early period of contact between the sorbent and the sorbate (Bai et al., 2001). Subsequently, the second reduction process play the main role in the period from 84 h to 108 hr because of the sharp increase of Cr (VI) and the removal process reached a relative equilibrium in 108 hr. Finally, between 84 hr and 108 hr of contact, the increase in percent removal and percentage reduction of Cr(VI) from the effluent is 97% and it will come to the saturation point in 108 hr at slowest phase.

4.8 ADSORPTION ISOTHERM ANALYSIS

The Freundlich isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems and is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where KF is a rough indicator of the adsorption capacity and 1/n is the adsorption intensity. In general, as the KF value increases the adsorption capacity of an adsorbent for a given adsorbate increases. Eq. (1) may be linearised by taking logarithms. The high magnitude of 'KF' and 'n' illustrate high adsorption capacity of free biomass over immobilized forms.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Conformation of the experimental data into Freundlich isotherm indicates the heterogeneous nature of the fungal surface. The equilibrium established between the adsorbed metal ion (q) and that remained unadsorbed in the solution (C) is represented by the Freundlich adsorption isotherm.

Table 4.3 Value of K_f (binding capacity), 1/n (binding intencity) and r^2(correlation coefficient)

Cromium Concentration (ppm)	K_f (bindig capacit)	1/n (binding intencity)	r^2(correlation coefficient)	Cromium Concentration (ppm)
100	676.0	0.48	0.97	100
200	501.18	0.49	0.94	200
300	100.0	0.34	0.92	300
400	48.11	0.29	0.99	400
500	33.88	0.24	0.91	500

The Freundlich constant, n also indicates the degree of favorability of adsorption (Treybal et al.,1981). Both the isotherms depend upon temperature. The Freundlich constant, n should have values lying in the range of 1 to 10 for classification as favorable adsorption (Rao et al., 2001; Raji et al., 1997). A smaller value of (1/n) indicates a stronger bond between adsorbate and adsorbent (Ramu et al., 1992), while a higher value for k indicates rate of adsorbate removal is high (Ajmal et al., 1998; Ramu et al., 1992). Hence it should be noted that the Isotherm constants are important in understanding the adsorption mechanism.

Figure 4.8 shows the maximum adsorption which is 75.55% in 72 hr. It was observe from the table 4.3, the binding capacity (k_f) on Chromium (VI) is higher 676.0, then any of the rest concentration and binding intensity (1/n) was higher 0.48 but less then 1.It indicates a stronger bond between adsorbate and adsorbent. Correlation coefficient (R^2) shows less redundancy in data from the central value. Higher the value of R^2 the better fit it indicates.

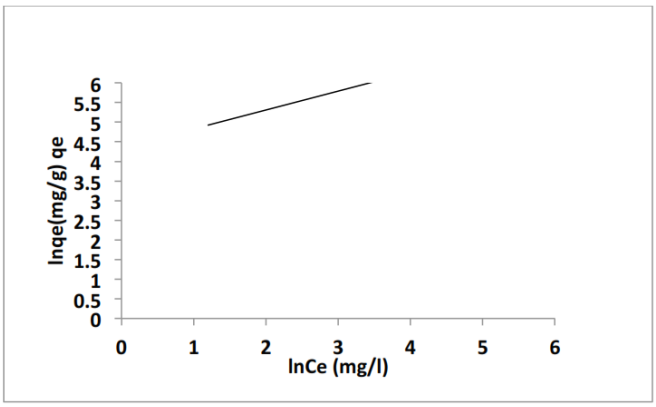

Fig 4.8 Freundlich fit for 100ppm

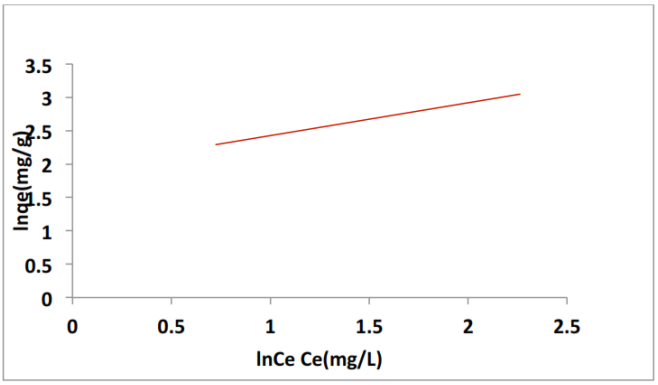

Fig 4.9 Freundlich fit for 200ppm

Figure no. 4.9 shows the maximum adsorption which is 71.0 % in 84hr. It was observed from the table 4.3, that the binding capacity (k_f) on Cr (VI) was 501.0 and did not vary if compared with the 100 ppm, It indicates that as the chromium concentration increased binding capacity will decreased here in this case binding intensity (1/n) is equal to 100 ppm 0.49 but less than 1 which indicates a stronger bond between adsorbate and adsorbent. Correlation coefficient (R^2) showed less redundancy in data from the central value. Higher the value of R^2 the better fit it indicates.

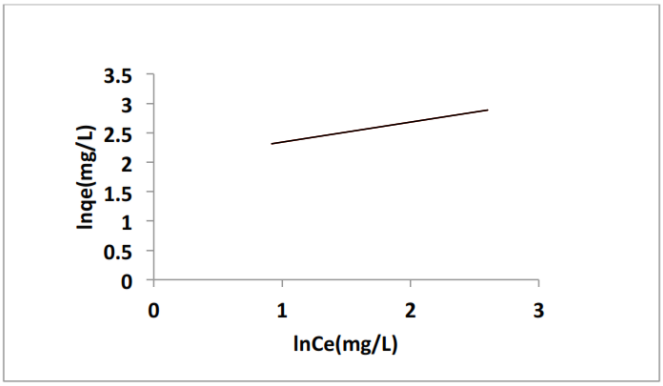

Fig 4.10 Freundlich fit for 300ppm

Figure no. 4.10, showed the maximum adsorption 70.37% in 72 hr. It was observe from the table 4.3, the binding capacity (k_f) on Chromium (VI) was 100, which indicates that as the Chromium (VI). concentration was increased binding capacity was decreasing, binding intensity (1/n) is lower then 100ppm 0.34 but less than 1. It indicated a stronger bond between adsorbate and adsorbent. Correlation coefficient (R^2) showed less redundancy in data from the central value. Higher the value of r^2 the better fit it indicates.

Figure no. 4.11, showed the maximum adsorption which is 97.88% in 108 hr. It was observed from the table no.4.3, we found that the binding capacity (k_f) on Cr (VI) is comparatively decreasing 48.11, but a drastic

decrease was observed in binding capacity of fungal biomass (in comparison the other Kf (values), which clearly indicated that toxicity level was increased which suppressed the growth of fungal biomass and it resulted in the drastic decrease in Chromium(VI) removal in early hr of incubation (72 to 84hr). Binding intensity (1/n) is lower than 100ppm 0.29 but less than.

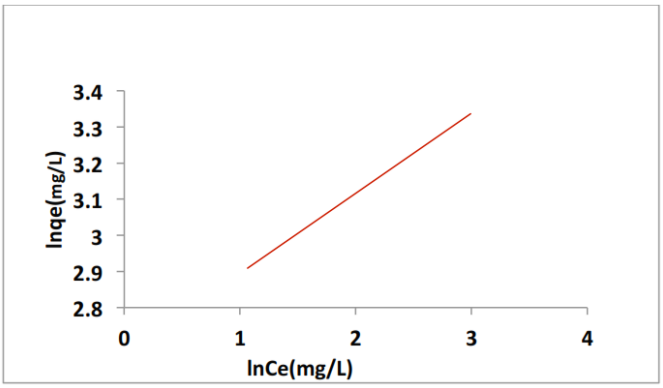

Fig 4.11 Freundlich fit for 400ppm

1. It indicates a stronger bond between adsorbate and adsorbent. Correlation coefficient (R^2) shows less redundancy in data from the central value. Higher the value of R^2 the better fit it indicates

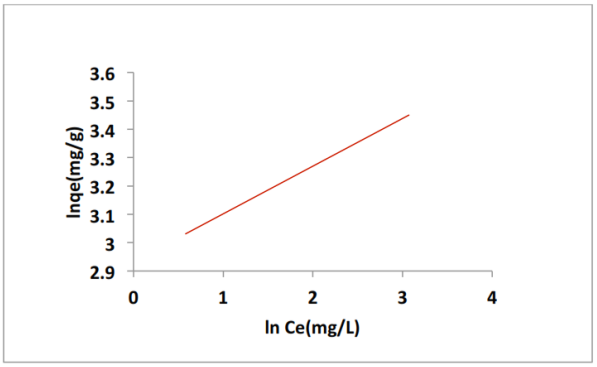

Fig 4.12 Freundlich fit for 500ppm

Figure 4.12, showed the maximum adsorption which is 95.56 % in 108hr. It was observed from the table 4.3 that the binding capacity (k_f) on Chromium (VI) was comparatively decreasing 33.88, but a drastic decrease in binding capacity of fungal biomass (as we compare the other KF values), which clearly indicated that toxicity level was increased results in suppressing the growth of fungal biomass and consequently decrease in Chromium (VI) removal in early hr of incubation (72 to 84hr). Binding intensity (1/n) is lower than 100ppm .24 but less than 1. It indicates a stronger bond between adsorbate and adsorbent. Correlation coefficient (R^2) shows less redundancy in data from the central value. Higher the value of R^2 the better fit it indicates.

V. Conclusion

Based on the result and discussion following conclusion are drawn.

- The discharge of Chromium (VI) into aquatic ecosystems has become a matter of concern in all the tannery areas in Bangladesh, this becomes a serious threat to the environment if not properly handled, and it can cause serious damage to soil and water bodies. The high amount of salt contained in the effluent, for example, can increase soil salinity, reduce fertility and damage farming in large areas. Tanneries also produce harmful gases, dust and a large amount of solid waste.
- The chromium removal efficiency depends on the viability of fungal biomass culture and concentration of chromium used and the mechanism of removal suppose to follow first order kinetics.
- The adsorption isotherm had been studied on the fungal biomass and Freundlich fit Of the adsorption data supported the surface heterogeneity.
- The chromium uptake rate found 805 mg/g, when 100ppm of chromium concentration was used in 72 hr. were as 2034 mg/g uptake in 500 ppm of chromium and the maximum binding capacity K_f observed in 100 ppm and minimum in 500 ppm.

• The fungal strain used in study showed good adsorption efficacy so for future works it is suggested to carry out few more studies at higher concentration of chromium.

References

[1]. Abou., S.R.A, Ghanem., K, Ghanem., N, Kalaiben., A.L, (2008), The role of bacteria on heavy metal extraction and uptake by plants growing on multi metal contaminated soils, World Journal of Microbiology and Biotechnology, vol. 24: 253 – 262.

[2]. Acevedo., A, Wrobel., F.A., Lokits., K, Caruso., K, Coreño., J.A, Alonso., A, Corona., G, Wrobel., J.F, (2008), Analytical speciation of chromium in in-vitro cultures of chromate- resistant filamentous fungi. Analytical Bioanalytical Chemistry, vol. 392 : 269-276.

[3]. Adekunle., I.M, Bangbose., O, Adetunji., M.T, and Lanre- Iyanda., Y.A, (2010), Impact of unremediated solid waste dumpsite converted to farmland on plant cadmium phytoaccumulation and toxicity, Journal of applied sciences in Environmental Sanitation, vol.27 : 226-238.

[4]. Ajmal., M, A., Mohammad, R., Yousuf., A, (1998), Adsorption behaviour of Cadmium, Zinc, Nickel and Lead from aqueous solutions by Mangifera Indica seed shell. Bangladeshn J. Environ. Health, vol. 40 : 15-26.

[5]. Anuradha., A, (2005), Adsorption of copper in sewage irrigated soils, Journal of Ecotoxicology and Environmental Monitoring, vol. 15 : 341-345.

[6]. APHA, AWWA and WEF, (2005), Standard methods for the examination of water ana waste water, 21st edition., Washington, DC, american public health association.

[7]. Aswathi., M, and Rai., L.C, (2005), Health effects of environment, Ecology and environmental safety, vol. 29 : 90-93.

[8]. Bai., R, Sudha., R, Emilia., A, (2001), Studies on chromium (VI) adsorption-desorption using immobilized fungal biomass. Bioresource Technology, vol. 87: 01.

[9]. Bai., R, Sudha., R, Emilia., Abraham, (2003), Studies on chromium (VI) adsorption- desorption using immobilized fungal biomass. Bioresource Technology, vol. 87 : 1.

[10]. Baldi., F, Vaughan., A.M, Olson., G.J, (1990), Chromium(VI)-resistant yeast isolated from a sewage treatment plant receiving tannery wastes. Applied and Environmental Microbiology, vol. 56 : 913–918.

[11]. Bernal., A, Ranes., C.S.M, Tapia., T, Olalde., N, Hernandez., J.T, and Dendooven., L, (2006), Effects of Tanneries waste water on chemical and biological soil characteristics, Applied Soil Ecology, vol. 33 : 269 - 277.

[12]. Bernal., A, Ranes., C.S.M, Tapia., T, Olalde., N, Hernandez., J.T, and Dendooven., L, (2006), Effects of Tanneries waste water on chemical and biological soil characteristics, Applied Soil Ecology, vol. 33 : 269 - 277.

[13]. Bernard., A, (2008), Cadmium and its adverse effects on human health, Bangladeshn Journal of Medical Research, vol. 128 : 557-564.

[14]. Deng., L, Zhang., Y, Jie., Q, Wang., X, Zhu., X, (2008), Biosorption of Cr(VI) from aqueous solutions by nonliving green algae Cladophora albida., Minerals Engineering, vol. 22 : 372–377.

[15]. Durai., G, Rajasimman., M, (2011), Biological treatment tannery waste water. Journal of environmental sciences and technology, vol. 1 : 1 -17.

[16]. Edday., N.O, Odoemelan., S.A, and Mbaba., A, (2006), Elemental composition of soils in some dump sites, Electtonical Journal of Environmental Agriculture and food Chemistry, vol.5 : 1399-1465.

[17]. Guidotti., T.L, Namara., M.J, and Mosses., M.S, (2008), The interpretation of trace element analysis in body fluids, Bangladeshn Journal of Medical Research, vol. 128 : 524-532.

[18]. Gupta., S, Satpati., S, Nayek., S, and Garai., D, (2010), Effect of waste water irrigation of vegetables in relation to bioaccumulation of heavy metals and biochemical changes, Environmental Monitoring Assessment, vol. 165 : 169-177.

[19]. Gupta., S, Satpati., S, Nayek., S, and Garai., D, (2010), Effect of waste water irrigation of vegetables in relation to bioaccumulation of heavy metals and biochemical changes, Environmental Monitoring Assessment, vol. 165 : 169-177.

[20]. Juan., F, González., Cárdenas, Ismael., Acosta, (2010), Hexavalent Chromium Removal by a Paecilomyces sp Fungal.

[21]. Korkina., L.G, (2007), Phenyl propanoids as naturally occuring antioxidants from plant defense to human health, Cell and Molecular Biology, vol. 53 : 15-25.

[22]. Mohanty., M.S, (1997), Raw hides and skin problem of procurement, curing preservation and marketing , presucted at CLRI, Madras.

[23]. Morales., L, Eliseo., B, Urbina., C, (2007), Hexavalent Chromium Removal by a Trichoderma inhamatum Fungal Strain Isolated from Tannery Effluent., Water Air Soil Pollut, vol. 187 : 327–336.

[24]. Nouri., M, Sepehr, S., Nasseri, M., Mazaheri A and Yaghmaian., K, (2005), Chromium Bioremoval From Tannery Industries Effluent by Aspergillus Oryzae., Iran. J. Environ. Health. Sci. Eng, Vol. 2 : 273-279.

[25]. Prasenjit., B, Sumathi., S, (2005), Uptake of chromium by Aspergillus foetidus, J Mater Cycles Waste Manag, vol. 7 : 88–92.

[26]. Raji., C, C, Anirudhan., T.S, (1997), Use of chemically modified sawdust in the removal of Pb (II) ions from aqueous media. Bangladeshn J. Environ. Hlth, vol. 39 : 230-238.

[27]. Ramírez., R, Calvo., R, Méndez, C., Avila, R, Lappe., M., Ulloa., P., Vázquez ., M, Juárez., R, Gutiérrez., J.F, (2004), Cr (VI) reduction in a Chromateresistant strain of Candida maltose isolated from the leather industry. Antonie van Leeuwenhoek, Vol. 85 : 63-68.

[28]. Ramu., N, Kannan., S, (1992), Adsorption of carboxylic acids on fly ash and activated carbon. Bangladeshn J. Environ. Hlth, Vol. 34 : 192-199.

[29]. Rao M., Parwate., A.V, Bhole., A.G, (2002, Removal of dissolved solids from textile mill wastewater by adsorption process. Journal of the IPHE, Bangladesh, vol. 2 : 37-44.

Khan Rajib Hossain. "Chromium Removal From Tannery Industry Waste Water By Fungus." *IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT)*, 13(2), (2020): pp 35-54.