Detection and Identification of Different Dyes and their Remediation from Tannery Wastewater by Adsorption Technique

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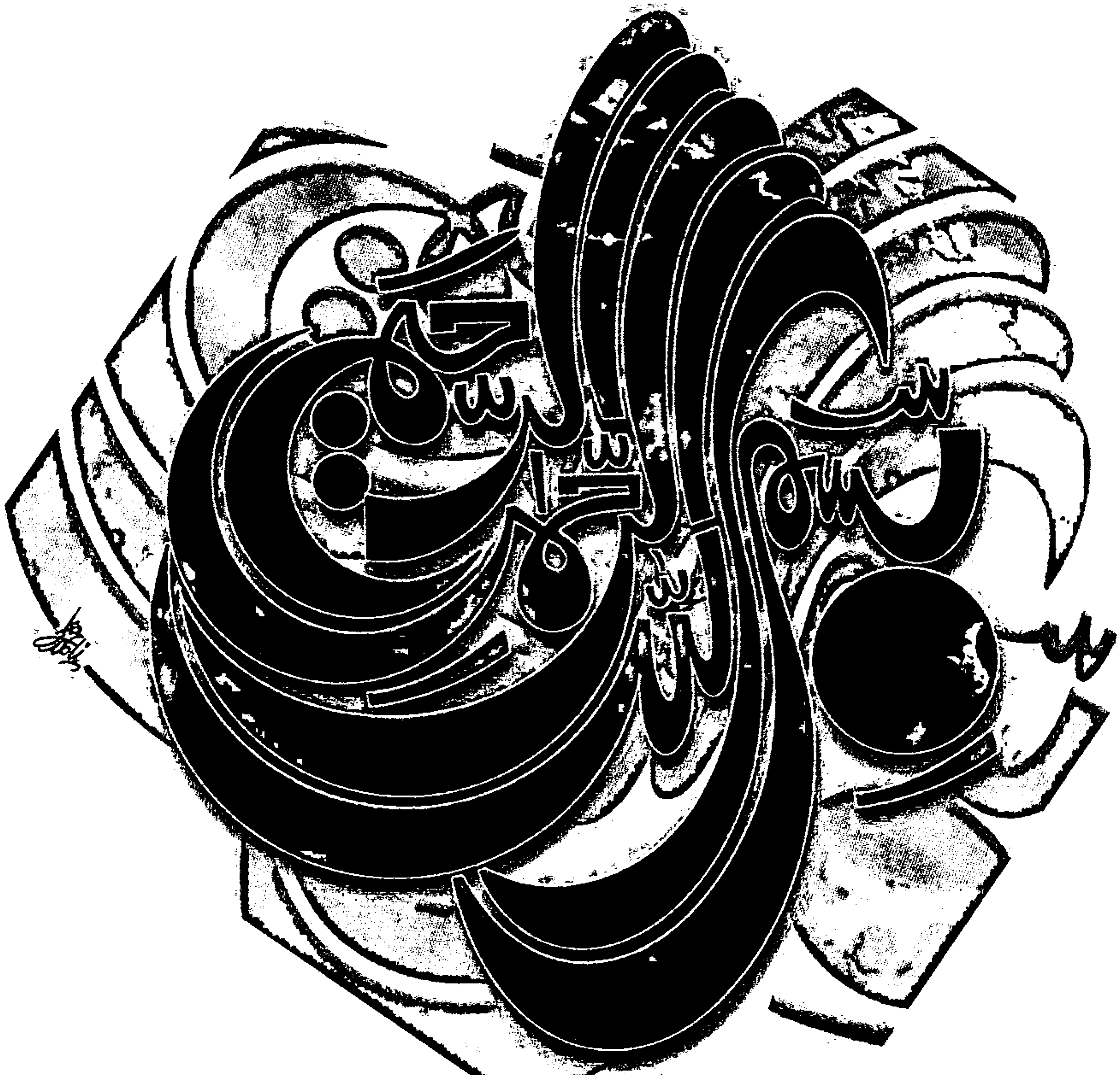
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FINAL APPROVAL

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To My Beloved Parents

DECLARATION

I hereby declare that the work present in the following thesis is my own effort, except where otherwise acknowledged and that the thesis is my own composition. No part of the thesis has been previously presented for any other degree.

Date ___________

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(Ammir Hamid)

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LIST OF ABBREVIATIONS

Acronym	**Abbreviation**
AAS	Atomic Absorption Spectrophotometer
AC	Activated Carbon
ACF	Activated Carbon Fiber
ACP	Activated Carbon Pellet
AOPs	Advanced Oxidation Processes
As	Arsenic
BOD	Biological Oxygen Demand
Cd	Cadmium
Cr	Chromium
COD	Chemical Oxygen Demand
Fe	Iron
GAC	Granular Activated Carbon
GDP	Gross Domestic Product
Hg	Mercury
IARC	International Agency for Research on Cancer

NEQS	National Environmental Quality Standard
Ni	Nickel
PAC	Powdered Activated Carbon
Pb	Lead
PEPO	Pakistan Environment Protection Ordinance
PNEP	Pakistan National Environmental Plan
TDS	Total Dissolved Solid
THMs	Trihalomethanes
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
Zn	Zinc

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ABSTRACT

The present study was carried out with a severe anxiety over huge environmental ruin being caused by the dyes and pollutants originating from indigenous tannery effluents of Kasur. Samples were collected from different sites of tannery area. In present study, Acid Blue 193 dye was identified from dye containing tannery effluent. Adsorption of an acid blue 193 was investigated by using activated carbon as adsorbent to find out its ability for removal of dyes from tannery wastewater because activated carbon is very well-known and easily available adsorbent and detection of various heavy metals like Cr, Cd, Zn, Ni and Pb were also performed from this dye containing tannery wastewater.

Adsorption study for the acid blue 193 dye was undertaken to study the effects of dose of activated carbon, initial solution pH, adsorption time, initial dye concentration and adsorption temperature. It was found that removal of dye is dependent on pH and maximum removal was 87.2% at pH 6. Dose of adsorbent was also found very effective against the dye removal and maximum removal was 81.9%. At initial dye concentration of 50 mg/L, maximum removal was 82.5%. As concentration was increasing, the rate of dye removal was reducing. When temperature was set 32.5 °C for adsorption of dye, then maximum removal was found 91.7%. Contact of time of adsorbent was also examined, it was found maximum when the time was set at 200 minutes and maximum removal was found 86.7%. It was also found that activated carbon can be feasible against the removal of all kind of dyes.

Atomic absorption spectrophotometer was used for estimation of Cr, Cd, Zn, Ni and Pb. The physico-chemical parameters like pH, temperature, conductivity, alkalinity, chloride, sulphate and sulphide was also determined. After the detection of these heavy metals, the overall mean of these metals was found by applying statistical tool. Mean of these metals in Kasur tanneries were following: Cr, 412.7 mg/L, Cd, 6.93 mg/L, Zn, 8.53 mg/L, Ni, 9.52 mg/L, and Pb, 11.59 mg/L respectively. Mean of all physico-chemical parameters was also find out which were following temperature, 30.17, pH, 5.8, total dissolved solid, 21815.2 mg/L, Conductivity, 51.35 mS/L, Chloride, 27595 mg/L, Sulphate, 3924.88 mg/L, Nitrate, 5613 mg/L, Calcium, 3719.48 mg/L and Chemical Oxygen Demand, 1804.88 mg/LO_2 respectively. The range of physico-chemical parameters was more than normal range.

The overall situation of distribution of these metals contributing significant harmful toxic properties. The effluent of tannery wastewater was contaminating groundwater, soil and environment of this area. It was found that it was releasing significant amount of metals and dye contents and these extreme concentrations of metals were becoming reason of many disorders for population of this area because amount of heavy metals was adversely exceeding from the safe limits. Mainly chromium level was extremely high then other metals. This study also demonstrated the role of activated carbon in dye removal and distribution and concentration level of heavy metals in tannery wastewater of Kasur tanning industry.

Chapter 1

Introduction

1.1 Preamble

Tanning is one of the oldest industries in the world. During ancient times, tanning activities were organized to meet the local demands of leather footwear, drums and musical instruments. With the growth of population, the increasing requirement of leather and its products lead to the establishment of large commercial tanneries (Durai and Rajasimman, 2011). In tanning process, animal hides and skin is converted into leather and associated products. Leather is a natural polymer consisting of collagen fibers cross-linked in a three dimensional structure by tanning substances. Conventional leather tanning results in an improved appearance as well as better physical, chemical and biological properties of the leather compared with the natural hide (Piccin *et al.*, 2012). The tanning process generates highly turbid, colored and foul smelling wastewater because the transformation of hides into leather is usually done by means of tanning agents.

In developing countries, rapid industrialization has impacted dramatically resulting in heavy losses to economic welfare in terms of their toxicological consequences on human health and ecosystem through water and air pollution (Reddy and Behera, 2006). Man-made pollution is affecting the natural worldwide water resources to such an extent that reinstatement to immaculate conditions is realistically impossible (Tornqvist *et al.*, 2011). More than 10,000 synthetic dyes were used for different kind of applications by various process industries (Ahmad and Rahman, 2011). These industries produce an enormous bulk of colored effluent carrying residual dyes which cannot be unconstrained without prior handling due to its toxicity (Deng *et al.*, 2011).

Developing agrarian economies, like Pakistan, require greater consideration in the context of problems linked with water pollution. Albeit the fact that leather industry is a leading economic sector in Pakistan, there is an escalating ecological apprehension concerning tanneries due to the production of large amounts of potentially toxic wastewater containing both trivalent and hexavalent chromium (Szpyrkowicz *et al.*, 2001). An example of rigorous water pollution induced by tanneries is in district Kasur, where half of the total numbers of tanneries (~300) in Pakistan are operational in close proximity to each other (Shakir *et al.*, 2012a). Effluent from the dyeing industry contain highly coloured species; such highly coloured wastes are not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological processes in water-bodies. Tanning industries in Pakistan are causing severe environmental problems due to the disposal of their untreated effluents on land and in water bodies.

1.2 Profile of Pakistan Leather Industry

The quick industrial progression in Pakistan has directed to severe issue of insufficient basic services and infrastructure i.e., unplanned industrial development, emergence of slums and transportation. In several areas particularly in cities where tanning industries are housed, there has been rapid deterioration of living conditions. Currently the mainstreams of occupants in these cities existing in un-planned, crowded localities made out of random industrial growth without acceptable public services and social facilities. It tends to become a source of intensifying problems as the tannery industrial sector grows bigger. Plans were prepared in the past to tackle the problem were directed more towards compulsions but seldom. Moreover, in the tanning industry development, environment management, research and training facilities remained practically nil (Rehman, 1999).

Nonetheless, amongst the manufactured goods sector, Leather of Pakistan and leather products industry is one of the key trades in exchange stipendiaries. Leather industry is performing a substantial role in the Pakistan's revenue and the leather and leather made-ups share in Gross Domestic Product (GDP) is 4%. At present 90 % of the leather is carry across in finished form. About 50 million hides and skins are managed each year. The leather industry in Pakistan is enduring to grow. In fact, the whole majority of industrialization quiet deceits gaining and it is predictable that the industrial development will twice in the next 10 years. No doubt that the leather tanneries would be a measure of this ever-increasing tendency (PNEP, 1991). In 1990, leather sector contributed 10.4 % toward the total export returns jumped to convert the second principal foreign conversation earner for the country (Shabbir, 1995a).

The impetus behind the increase in tanneries in Pakistan is a rising world demand for tanned leather. While the production of tanneries in the developed countries has grossly conic down due to either closure of tanneries or the leather produced there has become too expensive due to strict environment control laws, the developed countries have become more and more dependent on the supply of leather from the developing countries. This problem is immediately apparent when one researches the limited body of environmental guidelines for leather tanneries and the lack of enforcement of any existing environmental legislation (Iqbal, 1998).

1.3 Development and Present Status

The leather and leather product occupies a noteworthy place in revenue of Pakistan as cited above. The industry is now export oriented as apart from catering for domestic demands. More than 2500 tanneries (registered & unregistered) and footwear industrial units running in Pakistan. It has lately been described that there are approximately 700 registered leather-industrial units in Pakistan, which are manufacturing around 8 million hides and 40 million skins producing an annual progress of 1.5% and 3% respectively (Tahir and Naseem, 2007). There are some large, well mechanized, export oriented tanneries, especially in Karachi while small traditional and medium scale units are still prevailing. Nearby obtainable raw material (hides and skins) and bring in process chemicals are used mostly for leather production (Augustus, 1996).

Even different tanners in Pakistan have their own variants on the same basic process with the same raw material and finished products. The sequence of tanning stages is altered and the arrangement of chemicals, process temperature and the interval of states could be altered if some stages of tanning are deleted. There are alternative methods, i.e., manual or with varying degrees of mechanization of performing many specific stages because process variety may extend even further. The choice between them is mostly an economic question, the skill of labor, depending on prevailing percentage rates, the preferred scale of manufacture and product costs in various markets for finished leather (Shabbir, 1995b).

Leather treating up to wet blue (semi-finished) stage is earmarked for minor scale manufacturing. Making of footwear and constituents are also reserved for the small scale enterprises. These small divisions are family retained units hiring up to ten workers. Here very limited machines and equipment are used to carry out the operation. The ancient bag tanning method is still in practice although chrome tanning has replaced the slow vegetable tanning process to a great extent.

The leather product sector in Pakistan has other than 200,000 staffs and yearly growth rate of about 4.7 %. It is supposed that more than one million people contingent for their income on this sector if the cottage sector is included. In order to increase profits in this value-added sector, the industry is attempting to increase its production and export of the final product types. However, this will possibly only upsurge demand for the intermediary product in the country and thereby increase the contamination generated by tanneries. The Federal and Provincial Governments have responsibility for environmental control. Pakistan Environment Protection Ordinance (PEPO) 1983 is an essential anti-pollution ordinance and enables both Provincial and Federal legislatures to enforce regulatory measures.

Chapter 2

Review of Literature

2.1 Introduction

Literature relevant to tannery industry and removal of dyes from dyes wastewater was reviewed comprehensively.

2.2 Environmental Aspects

In Pakistan's leather industry, the extensive release of raw wastes from tanneries is a growing problem. As increase of tanneries in Pakistan, the unprocessed effluent of tanneries is affecting severe environmental degradation because after releasing into nearby natural water bodies it ultimately reaches the sea. In addition, due to tanneries burning residuals (i.e. hair) from the tanning process, the air pollution is on the rise. While at the same time, strict environmental regulation is not implemented because the tanning industries are given export rebates. Delicate stability is present between the Pakistani leather profession and the atmosphere because the blend of a growing request for the leather manufacturing and a deficiency of government instruction is impairing.

Subsequently, the correlation between environment and the Pakistani leather trade is being stressed by a rising orders for the leather product in the world and unawareness of environmental difficulties resultant from the tanning procedure. It is assessed that a only one tannery disposes around 15,000 tonns of chromium sulfate and 40,000 tonns of elementary chemicals and effluents per annum, which extremely upsets the ordinary environment (Tariq *et al.*, 2005; Galiana-Aleixandre *et al.*, 2011).With rare land assets, the pollution is affecting large numbers of people and imparting a detrimental effect upon their health because the tanneries are located in residential areas

2.2.1 Pollutants generated by tannery effluents

The primary pollutants like dyes, heavy metals, several organic chemicals and acids are generated by that leather tanning in Pakistan. It is verified that effluent runoff from leather tanneries have been found toxic. A variability of chemicals is used during the tanning process in a tannery unit holding huge quantity of organic and inorganic composites like normal and artificial tannins, sulfonated oils, dyes, surfactants, biocides, organic acids , acrylic resins, ammonia, chromium (Cr), sulfide and chloride (Costa *et al.,* 2008). The extremely colored dye solution released to the environment is appealingly undesirable and would reason harm to the ecosystem and aquatic living creatures since dyes delay light diffusion and interrupt biological progressions in water. Some dyes are toxic and harmful for human being and are highly carcinogenic to human health. Due to robust confrontation to light, pH and microbial decay, most dyes contents in wastewater are non-biodegradable. The concentration sorts for parameters such as biological oxygen demand (BOD), suspended solids, chemical oxygen demand and sulfide are comparatively sophisticated for vegetable tanning than for chrome tanning in accumulation to chromium and total dissolved solids.

2.2.2 Harmful environmental effects of tannery wastewater

The poor treating practices further aggravate the pollution problem due to use of untreated conservative leather treating approaches. Due to the presence of sulfide in the effluent, dyes, chromium and hydrogen sulfide formed which are highly toxic to various forms of life. It is as well identified that small pH of tannery wastewaters reason erosion of the water carrying systems. Moreover, high Biological Oxygen Demand (BOD) and large fluctuations in pH values may kill all natural life in a contaminated water body. Tanneries are polluting the major agricultural lands directly in addition (Ramasami *et al.,* 1997). A number of inquiries have exposed that the food produced is polluted and the crop product have been harmfully affected. The other environmental effects of tannery wastes contain the smell of rotting flesh near the tanneries, the overgrazing of cattle, the ammonia and flue gas emissions from unhairing and fleshing and the odor of sulphide emissions from the unhairing. These are also recognized to cause the damage of land efficiency and obstruction of propagation of plants and seeds. The allergies and cancers are caused by leather dust that injures the local inhabitants near the tanneries (Pojer and Huyneh, 1999).

Leather industry release mutual mangrove obliteration and over-fishing are causative to a sharp reduction in shrimp production. The mangroves whose leaf disorder is a main cause of nutrients deliver a different habitation for a multifaceted and symbiotic communal of invertebrates, birds, fish and reptiles. In addition, almost 90 % of hot marine species pursue housing in the mangroves for one phase of their life cycles (More *et al.*, 2001).

2.3 Effluent Quality Parameters

The outcome of extreme contaminant heights usually initiate in the tannery effluents can be harmful: specific quality determining physico-chemical parameters that designed the basis of the current study are described now.

2.3.1 Solids

The solids present in tannery effluents drop into numerous diverse types. The suspended solid causes a variety of problem when discharged from site due to its insoluble material components because they are made up of solids with different features.

2.3.2 Settleable solids

These can be seen in suspension when an effluent sample is shaken but settles when the sample is left to stand because of comprise material. The main stream of these solids settles down within 5 to 10 minutes. While some fine solids need additional time to settle. These solids create from all steps of leather production they include adequate leather particles, excesses from several chemical ejections and reagents after diverse waste liquors. Huge quantity is made through beam house methods.

2.3.3 Semi-colloidal solids

These are another form of solids which does not settle down from an effluent sample even subsequently being left to stand for a substantial duration of time. However, they can be strained from the solutions. Furthermost of these solids are protein remainders from liming process and the beam house operations. However, enormous extents are also produced in arrears to deprived application in vegetable tanning process. Semi-colloidal solids can be broken down over an extended time by bacterial digestion producing solids which will eventually settle because these do not directly cause a sludge problem.

2.3.4 Gross solids

Gross solids are present in huge quantity as compared to other solids. The waste constituents that give growth to this type of solids are often trimmings and shavings, solid hair debris, fleshing residues, large pieces of leather cuttings and remnants of paper bags. By means of coarse bar screens set in the path of wastewater flow, these solids can be simply detached.

2.3.5 Oxygen Demand — BOD and COD

Through bacterial action many constituents in wastes are fragmented into further simple constituents. O_2 is obligatory for the breakdown of the components and existence of these bacteria (aerobic bacteria). This breakdown can be quite rapid or may take a very long time to depending on their composition.

Biochemical Oxygen Demand (BOD) is the very significant and extensively used environmental key for observing organic pollutants in wastewater (Pasco *et al.*, 2004). This method of exposure has various restrictions: the analysis is a highly sensitive process and the bacterial cultures can vary. During the preparation and the analysis itself, the results can be ambiguous if the most stringent care is not taken. Many effluent components take longer than the period of study to analysis while BOD is the measure of the oxygen obligation of bacteria under controlled conditions. Certain chemicals will only be moderately broken down although other may not be expressively harmed during the time.

Naturally vegetable tanning waste has a long break down duration which is frequently mentioned as being up to 20 days. These extended digestion periods can put on to a variation of chemicals used in manufacturing leather including some synthetic fat-liquors, dyes and residual proteins from their solubilization and certain retanning agents. As the wastewater components are carried greater distances before breaking down and this extensive breakdown period means that the environmental influence is spread over a larger area.

Chemical Oxygen Demand (COD) is one of the utmost essential parameters and has been widely used to show the organic pollution in aqueous systems (Mu *et al.*, 2011). The parameter of COD find out the oxygen compulsory to oxidize the effluent samples exclusively. It sets a worth for the constituents that would usually be digested in the BOD examination as well as the chemicals that remain unaffected by bacterial activity and the long-term biodegradable products.

2.3.6 Nitrogen

Nitrogen is controlled in numerous altered components of tannery effluents as a portion of their chemical structure. The most common chemicals are the proteinacious materials (from liming/unhairing operation) and ammonia (from deliming materials). These bases of nitrogen create two direct problems. Firstly, the plants have need of nitrogen for their growth but the high levels released by substances covering nitrogen overstimulated the progression. Watercourses become blocked and streams compromised due to the quick growth of water-base plants and algae. An excessively large amount of organic matter has to be broken down when the plants die. If the load outstrips the natural supply of oxygen from the river, ultimately anaerobic surroundings develop plants, fish and aerobic bacteria die and secondly, the nitrogen free through deliming process and protein break down is in the form of ammonia. Bacteria can change the latter over numerous stages into water and nitrogen gas which is eventually released into the air. Both of these break down's yields are non-toxic but yet great amount of oxygen is required in the process. Toxic and aerobic conditions may rapidly develop if oxygen request is more than the smooth abounding obviously from watercourse.

2.3.7 Sulphide

The sulphide content in the tannery effluent results from the use of sodium sulphide, sodium hydrosulphide and the breakdown of hair in the unhairing process. The sulphide contains various problems. The sulphide remains largely in solution under alkaline conditions. Hydrogen sulphide evolves from the effluent when the pH of the effluent drops below 9.5. When the rate of evolution of hydrogen sulphide is increased then the pH becomes low and it is characterized by the odor of rotten eggs, so a severe smell problem takes place. Due to certain bacteria in the rivers, sulphide can be oxidized into non-toxic compounds. However, this creates the higher oxygen demand that can harm aquatic life. Sulphide in open drain can pose structural hitches due to erosion by sulphuric acid produced as an outcome of microbial exploit.

2.3.8 Sulphate

The sulphate is a constituent of tannery effluents originating from the usage of sulphuric acid or produces with high sodium sulphate content. Several supplementary chemicals have sodium sulphate as a by-product of their production. For example, chrome tanning powder holds great intensities of sodium sulphate as do many chronic agents. Sodium chloride affects fresh water life when its concentration in stream or lake becomes too high but it has no effect when discharged into estuaries or the sea. Accumulation of sulphate causes decomposition to existing configurations.

2.3.9 Chloride

The sulphate content runs below 1000 mg/L but chloride content of tannery composite wastewater ranges from a few thousands to tens of thousands mg/L (Shabbir, 1995a). The high levels of chloride can lead to breakdown in cell structure and inhibit the growth of plants, bacteria and fish in the surface water. Surface salinity rises through evaporation and crop yields fall if the wastewater is used for irrigation purpose. Chlorides re-enter the ecosystem when flushed from soil by rain and may eventually end up in the groundwater. If the effluents are discharged into marine environment then high salt contents in effluent are only acceptable.

2.3.10 pH

The acceptable range of pH for both wastewater and surface water is vary from 5.5-10. Although severe limits are frequently set but sometime greater acceptance is shown towards higher pH since carbon dioxide from the atmosphere or from living processes in healthy surface water systems inclines to lower pH levels very successfully to impartial conditions. Complex fish and plants lifecycle are disposed to harm if the apparent water pH shills too far each way from the pH range of 6.5-7.5.

Municipal and common treatment plants prefer to discharges additional alkaline as it decreases the destructive properties on concrete. Hydrogen sulphide evolution is minimized because metals tend to remain insoluble and more inert. The pH is dropped to extra impartial surroundings by CO_2 thus changed after natural developments are comprised by means portion of the handling.

2.3.11 Chromium

The compounds of metals are not decomposable. They can thus be viewed as long-term environmental threats. The tanning industry is a renowned source of Cr pollution in addition to other industries such as dyeing, metallurgy, coke, ceramic, cement and asbestos. This is precisely accurate for soil pollution rising from extreme Cr levels in the washout fluids from these industries (Kabata-Pendias and Pendias, 1979; Hekstra, 1995). The metal occurs under normal conditions in Cr(III) and Cr(VI) forms but the redox chemistry of Cr makes it an imperative metal from the view point of pollution. This offers prospect for Cr(III) and Cr(VI) transformation and back. In aqueous and soil media numerous workers have done dynamic research work on the redox couples of Cr(III) and Cr(VI) systems. Precisely such an attitude deals the understanding about formal redox aptitudes and the mechanism that is complicated in the speciation of the metal to understanding the distinct part of Cr(III) and Cr(VI), the last being assumed to be carcinogenic (Rathindra *et al.*, 1996).

Cr(III) and Cr(VI) are two forms of chromium which are linked with tanning industry. Cr(III) is displaced from leathers during both retanning and dyeing processes but mainly found in waste from the retanning system. The precipitates containing mainly protein-chromium complexes are formed because this chromium in soluble form reacts very rapidly with protein containing wastewater from other processes. Tannery wastes are improbable to enclose Cr(VI) in the form of dichromate. Dichromates are swiftly penetrating cell walls so that it is toxic to fish life. According to the United States Environmental Protection Agency (USEPA), the allowed amount of Cr(VI) and total chromium released to surface water should be less than 0.05 mg/L and 0.1 mg/L respectively but tanneries normally discharge chromium in hundreds mg/L (Baral and Engelken, 2002).Whereas the National Environmental Quality Standard (NEQS) recommended value demands just 1.0 mg/L for quality assurance of chromium in wastewaters but it has been perceived that contaminated water of chrome tanning procedure that is around 2% of the entire wastewater of the tannery contains as high as 6000-7000 mg/L of chromium (Baruthio, 1992).

2.4 Health Effects of Some Wastewater Related Metals

Research has shown that the fitness situations of the populations are poor in the contaminated area with a high incidence of such symptoms as weariness, dizziness, dermatitis, poor appetite and abdominal pain. The chromium content in the urine of subjects in the polluted area (about 0.12 pmoles/L) is much higher than that in the control area and the blood pressure of the inhabitants of these areas is generally lower than that of control area (Parikh *et. al.*. 1995). The probable hostile effects of chromium in industrial contact of tannery workers have recommended that chromium has a harmful effect on the iron metabolism linked with extreme body chromium metabolism and the dust produced during several processes have remarkably adverse effects on the nose, throat and lungs (Packham, 1996).

In the tanning process, metals are important constituents of chemicals. Therefore, a huge amount and various kinds of metals are present in tannery wastewater. These suspended particulate and sediment metals made rapidly partition as dissolved and deposited in water (MacKay and Diamond, 2003). Maximum of the metals, particularly in lakes and reservoirs linked with the sediment though the residue acquaintances with the particulate and liquefied phases in changing ratios contingent upon the volume of suspended matter. Due to their lethal effects on human health, the naturally occurring heavy toxic trace metals in soil and water are well known.

There are some non-essential metals but some metals are essential for proper functioning of the living organisms are known to be toxic even at actual low levels, for example Lead (Pb), Mercury (Hg) , Cadmium (Cd) and Arsenic (As). Whereas Zinc (Zn) and Copper (Cu) are the metals that are biologically necessary but it can also become hazardous at great levels. Nonessential metals contain potential to interfere with the typical functions of cell because it is suspected to enter metabolic pathways of chemically similar essential elements. In return, important elements can transform the harmful effects of the lethal elements.

Metal-metal competitions like cadmium-zinc or cadmium-iron interfaces are the acute modifiers of the metal toxicity and are the well documented example (Jarup, 2002).

As with whole harmful agents, absorption at the site of interaction, elimination, metabolism and distribution are the main steps that regulate the actions of the metals. Skin contact may characterize a way of endorsement of various metallic compounds specifically the lead enclosing compounds but the trace metals move in human body mostly subsequent oral or pulmonary contacts. The most dangerous sun stable metal elements are those that have ability to pass the pulmonary epithelium. Some other metals like cadmium adopt this way of absorbance and openly reached to the central nervous system. Nickel (Ni) is also present in tannery effluent which is important element that can be lethal and can cause carcinogenic in high concentrations. Contact to Ni compounds causes irrevocable harm to the cardiovascular system, central nervous system, gastrointestinal tract and lungs (Axtell *et al.*, 2003). Nickel has been categorized between the crucial micronutrients and remains linked with various metallo-enzymes (Srivastava *et al.*, 2005).

Cadmium pollution of groundwater and soil is a universal environmental problematic which shows danger on both environment and public health. Due to its high water solubility and toxicity, cadmium is a substantial metal pollutant in the environment. Permissible limit for cadmium in drinking water is 0.003 mg/L because it is an effective neurotoxic metal (Government of India, 2000). Cd(II) is known to cause hypertension, bone degeneration, renal dysfunction, liver damage and lung inefficiency in humans due to its extreme toxicity. Cd (II) has been contained within the black list of EEC Dangerous Substance Directive (EEC black list substances, 1976) and red list of significance pollutants by the Department of Environment, UK (UK red list substances, 1991) on the basis of its adverse health effects. Cd (II) is classified as group B1 carcinogen by US Environment Protection Agency has also classified (US Environmental Protection Agency, 1999). International Agency for Research on Cancer (IARC) has declared the cadmium as category I carcinogen. Cadmium is actuality known as most contaminated metal from three most dangerous metals. The other two metals are lead and mercury, which are also responsible for toxicity in aqueous environment. These metals have penetrated in food chain and have become adverse threat to human health.

Similarly, Zinc (Zn) is an important metal because it has enzymatic and structural important role in regulatory and biological system. Extreme exposures of zinc can origin gastro-intestinal distress, pancreatic damage, anemia and diarrhoea. It has many severe and chronic effects on human health like osteomalacia, renal dysfunction/nephropathy. Inhalation of zinc fumes may cause neurological destruction often called metal fume fever and flu-like indications. Long period exposure may outcome in lung cancer (Aggett and Comerford, 1995).

Iron (Fe) is also a significant metal. Lethal effects are demonstrated with overdose of iron that results in metabolic acidosis, toxic hepatitis, gastro-intestinal upset/lesion and shock. Inhalation of iron may generate pulmonary siderosis while its overload causes hemachromatosis and hemasiderosis, liver cirrhosis and cancer. Contaminated effects of magnesium are associated to magnesium oxide. Its severe effects by inhalation result in dangerous effects contain Parkinson's disease and pneumonitis. Being a portion of vitamin

13ꜝ2, cobalt is a critical nutrient. The inhalation of high levels of cobalt causes asthma, pneumonia and wheezing after affecting the lungs (Goyer, 1996). There is no doubt that Cr(VI) compounds are both acute arid and chronically toxic although essentiality of chromium is still controversial. Probably due to the low solubility of trivalent form of Cr(III), it is less toxic than some other elements (Hg, Cd, Pb, Ni and Zn) to mammalian and aquatic organisms. Skin irritations may be caused by High doses of Cr(III). Long term exposure of Cr(VI) by inhalation causes nasal frustration and lung disorder while the short term exposure at high levels causes irritation and ulcer at the site of contact (Bosnic *et al.*, 2001).

2.5 Dyes

Dye is an organic compound that tells colour to substances such as leather, textile fiber, plastic materials, wax, hair or either is solution or dispersion (Zollinger *et al.*, 1991). In the prehistoric times, dyes were derived from natural plants by the man mainly for colouring fabric. But now a day, all dyes are artificially produced including natural dyes. The artificial dyes are considerately defined to have unique characteristics such as; resistance to fade when exposed to light, chemicals and washing, ability to impart specific colour to the substance (Ozcan *et al.*, 2007) and confrontation to acids and bases. The groups called auxochromes (NO_2, NO, N=N) have modified the ability of chromophores to absorb light. Chromophores (OH, NH_2, NHR, NR_2, Cl and COOH) are the part of molecules which are responsible for the colour by adsorbing wavelength. Dyes can be generally classified in two ways either depend upon application or chemical composition.

2.5.1 Dyes and Water Pollution

The dyeing industries contain highly toxic pollutant. It is necessary to removal dye from tannery wastewater before its release (Acemioglu, 2004). Various industries are using significant amount of dyes. Due to non-biodegradability and high toxicity of these compounds, these are causing severe damage to the environment.

Dyes are used as a coloring agent for various different substances and also have a wide range of other application. Dyes are extensively used to impart colour to plastics and fabrics (Zollinger *et al.*, 1991). They are also used in leather industry, printing and food industry (Srinivasan *et al.*, 2007). The popularity of dyes has increased in another field recently that is in hair coloring (Khenifi *et al.*, 2007).

2.6 Methods to remove dyes

Most of dyes are known to be non-biodegradable. Some investigations have focused on the development of biological and advanced oxidation processes for treatment process of dyes containing wastewater. For the former, it has been originate that it may be effective in the reduction of COD and removal of suspended solids but is largely useless in eliminating colour from wastewater. The dye wastewater cannot be proficiently purified and treated because of the huge organic concentration and composite composition of dye wastewater. Many chemical and physical processes have been applied for colour removal of dyes including physiochemical, biological, membrane filtration, flocculation, advanced oxidation biosorption and coagulation and (Ma *et al.*, 2011; Madaeni *et al.*, 2011; Verma *et al.*, 2012; Whang *et al.*, 2012).

2.6.1 Physical methods

2.6.2 Adsorption

Adsorption is a famous stability separation process and an actual technique for water sanitization applications (Dabrowski, 2001). The word adsorption mentions to a process wherein a material is intense with gaseous surroundings or at a solid surface from its liquid. Due to adsorption process simplicity and performance, it has developed as a possible substitute for the treatment of such colored wastewater (Mona *et al.*, 2011; Asgher and Bhatti, 2012). The material that is present on the surface is called adsorbate and the constituent on which it adsorbs is called adsorbent. Adsorption takes place due to the alteration in the characteristic of surface of the adsorbent then the bulk. The free valances at the surface or destabilize inward force of attraction has property to entice and hold the molecules onto surface with which they originate in contact (Jiuhui, 2008).

When Van der Waal forces hold the molecules of an adsorbate on the surface of adsorbent without subsequent into the establishment of any chemical bond among them is called physical adsorption. This sort of adsorption is considered by small heat of adsorption about -20 to 40 kj mol/L. Physisorption is commonly rescindable in environment (Treybal, 1981). When formation of a chemical bond takes place between molecules of adsorbate are detained on the surface of an adsorbent is called chemical adsorption. It is also called as chemisorptions or Langmuir adsorption. This form of adsorption develops extra heats. Chemisorptions is typically irreversible process in nature (Treybal, 1981; Jiuhui, 2008). It is broadly used for the confiscation of color from dye effluent, oils, edible and sugar industry. Trihalomethanes (THMs) which are toxic and carcinogenic can also remove by adsorption technique.

Adsorption process can work individually for the eradication of colour. Organic compounds that are chemically and biologically established can be degraded by this process (McKay, 1996). Parameters like adsorbent dosage, initial dye concentration, temperature affect the adsorption of dyes from dye effluent and contact time is associated with an adsorption process. Furthermore, adsorption isotherms is used to find out equilibrium association between the quantities of dye adsorb on the surface of an adsorbent (Bulut *et al.*, 2008).

Adsorptive removal of dyeing waste color has many advantages because of its insensitivity to toxic substances, simplicity of process design, blow cost and ease of operation (Garg *et al.*, 2004). Adsorption has significant linking through ecological and social care due to removal of toxic materials, hazardous ions and dyes from industrial effluents. Numerous adsorbents are suitable for such tenacity.

After adsorption, high quality of effluent is generates (Nandi *et al.*, 2009). The pollutants present in the wastewater attribute to the surface of the adsorbent during this process. This collaboration between the adsorbate and the adsorbent can be manifest by physical properties and adsorptive characteristics (Lian *et al.*, 2009).

2.6.2 Coagulation

Coagulation is a conventional physico-chemical method use for the treatment of the water. Alum and iron salts use as coagulant and added to wastewater to enhance the ability of the tiny particles to conjugate (Martines-Hutile and Brillas, 2009). Only coagulation cannot be used for the elimination of contaminants from wastewater. It needs following processes such as filtration, sedimentation and disinfection (Letterman, 1999).

Still, to the extent that which is identified, no efforts are done to entirely examine the optimization of coagulation in aggregation with sequential biochemical treatment of contaminated tanning effluents. Each coagulant shows maximum pollutant removal at an optimum pH and works most efficiently in a specific pH range. The features of the tannery effluent along with the amount of coagulant are very important for the effectiveness of pH range and used coagulant.

2.6.3 Filtrarion

Various particulate matters present in the wastewater and filtration process are usually applied to remove them. Membrane filtration has great ability to remove the dyes from wastewater. Most prominently membrane filtration can be used for the incessant exclusion of dyes from dye containing wastewater (Xu and Lebrun, 1999). Filtration is resistant to microbial attack, temperature and chemicals also because it is different from other physico-chemical methods. The dye wastewater treated by filtration process is not feasible but it can be used within leather industry (Mishra and Tripathy, 1993). The formation of sludge during treatment is a major problem (Letterman *et al.*, 1999). In adding, filtration contains tendency of membrane to clog and high capital cost which affects the performance of filtration procedure (Robinson *et al.*, 2001).

2.6.4 Ion exchange

An ion from solution is replaced for a similarly charged ion involved to an immobile solid particle is called ion exchange. It is mainly an alterable chemical process. Ion exchange (LeVan *et al.*, 1997) contain many collective structures laterally through adsorption in respect to use in fixed-bed and batch procedures because these could remain assembled composed as sorption processes for a combined treatment to have reasonable water condition. Ion exchange is a feasible method for the removal of colours from waste.

For the removal of dyes, various studies have been performed by using ion exchange (Wu *et al.*, 2008a: Raghu and Basha, 2007; Liu *et al.*, 2007). Delval *et al.*, (2005) made starchy polymer by cross linking reaction of enriched flour and starch with epichlorohydrin as a cross linking agent in the presence of NH_4OH. Authors found an association between the structure, movement and degree of cross linking of these sorbents when they examined about structural properties of cross linked starch materials, the yield and mobility with various compositions. For the retrieval of a number of dyes from aqueous solutions, these cross linked starch-based materials having tertiary amine groups were used. The authors recommended that the sorption mode of action was interrelated to the polymer structure. No loss of sorbent and the availability of wide variety of resins for precise application are the benefits of ion exchange.

2.7 Chemical methods

2.7.1 Oxidation Process

The process in which oxidizing agents are used to treat wastewater is called oxidation. Generally, it has two forms. Hydrogen peroxide, potassium permanganate, ozone and fenton's reagent are used for treating the emissions and chemical oxidation and UV assisted oxidation via chlorine, specifically those acquired from primary treatment. It requires small extents and little response periods so that these are among the most frequently used approaches for decolourisation processes. These can be used to completely or partially to degrade the dyes which have lower molecular weight species such as carboxylates, aldehydes, nitrogen and sulfates (Gupta and Suhas, 2009). Conversely, whole oxidation of dye can hypothetically moderate the composite molecules to carbon dioxide and water. It is worth to consider that pH and catalysts has a vital part in oxidation process. It can be boosted by using catalysts and through regulate of pH e.g., in the decay of metal-compound dyes metals, like copper, nickel, chromium and iron are unconventional and these metals contain catalytic consequence that raises the removal of dyes.

2.7.2 Sodium hypochlorite

Chlorine is known as a robust oxidizing agent and may also be useful as calcium hypochlorite and sodium hypochlorite. It is broadly used for reduction of colour like leather, textile bleaching and pulp because it is most usually used as decontaminator for water treatment. Water insoluble vat and disperse dyes show resistance against removal of dyes during this process but various dyes include acid, reactive, direct and metal complex dyes are water soluble and can be decolourised freely by hypochlorite (Namboodri *et al.*, 1994a; Namboodri *et al.*, 1994b). It has been reported that metal complex dye solution residues moderately coloured even after an extended period of treatment while decolourisation of reactive dyes generally need extensive reaction periods. It is most susceptible to chlorine and easily decolourise the dye if naphthalene ring (Omura, 1994) contain amino group or substituted amino groups. Although chlorine gas is very low cost technique for removal of dyes from wastewater but it has also very harmful effects because the metal release during the metal complex may become reason of corrosion in metallic vessels and growing the absorbable biological halogens content of the treated water due to production of organochlorine compounds including toxic trihalomethane.

2.7.3 H_2O_2-Fe (II) Salts

Hydrogen peroxide (H_2O_2) is slightly more viscid than water and actual pale blue liquid which looks colourless in a dilute solution. It is a strong bleaching agent due to powerful oxidizing properties and used for bleaching paper moreover other uses. In 1994, around 50% of the world's manufacture of hydrogen peroxide was used for leather, pulp bleaching and paper (Hage and Lienke, 2006). Peroxidase enzymes are generated from hydrogen peroxide which is used for removal of dyes from wastewater (Morita *et al.*, 1996).

Although this method completely depends upon pH and sludge which is produce during this reaction. Fenton's reagent is solution of iron catalyst and hydrogen peroxide but it is powerful than hydrogen peroxide used to oxidize dye wastewaters (Meric *et al.*, 2003; Wang, 2008). Generally, it is active (Kim *et al.*, 2004) in removal of dye colours both insoluble and soluble dyes though certain dyes like disperse and vat were originate to be strong to it. It is to be observed that not only colour is removed but total organic carbon and toxicity and COD is also reduced. The method is feasible for wastewater treatment when a municipality allows the discharge of Fenton's sludge into sewage with high concentration of suspended solid. From a biological perspective, it is supposed that the phosphates can be eliminated with the improvement of the sludge. The leading disadvantages are that it is frequently actual within slight pH sort (Cheng *et al.*, 2004) of <3.5, includes sludge production and takes slower reaction time.

2.7.4 Ozonation

Ozonation is basically an oxidation method and efficiently used for removing artificial dyes (Forgacs *et al.*, 2004). During ozonation process, conjugated double bond (-N=N-) is degrade linked with dyes and responsible for the colour of dye (Srinivasan *et al.*, 2009). In the recent years, chemical oxidation with ozone is Advanced Oxidation Processes (AOPs) which is getting attention to enhance the presentation of the natural handling procedures by refining the biodegradability without formation of sludge. Recent studies indicate that ozonation measured as an initiative to the natural practice to improve the ability of biological dealing which increases the biodegradability index of the effluents and permits removal of dye colours as well (Preethi *et al.*, 2009). Pre-ozonationhas been used for the tannery wastewater earlier anaerobic treatment to keep final BOD and COD within the recommended parameters. Post-ozonation of the anaerobic treatment has also been exposed the colour and turbidity removal, virus and bacteria removal in the final release in stream and reduction in smell in the open environment (Balakrishnana *et al.*, 2002). Apart from pre-ozonation and post-ozonation, ozone can produce reasonable results within biotreatment as a mid-treatment stage (Dogruel *et al.*, 2006). It can be a promising technique for the tannery wastewaters after chromium removal because of its exceptional features such as easily operated and decomposition of residual ozone, no sludge formation, disinfection property and possibly feasible for both colour confiscation and organic decrease in one phase (Houshyar *et al.*, 2012).

2.7.5 Photocatalysis

Photocatalysis is very important and effective process used for treatment of organic pollutants. It is a process in which semiconductor absorbs the photon which escorts to the configuration of electrons and gaps. Semiconductors contain a region among the top of the valance band and bottom of the transmission band known as band gap. For the combination of electron, no energy is present in this region. Incident photons recombination generates most electron hole pairs before they can attain the shell and may also modify at the surface of semiconductor (jiang *et al.*, 2004). As a result, photo activation produces a hole. Thus, to get over this energy gap, photon power, hv, equivalent to or further then the band gap is necessary to stimulate an electron (e^-) from the valance band to transmission band. A positively charged hole (h^+) in the valance band is generated when the electron moved toward the conduction band. Usually, ultraviolet photons are necessary to perform this reaction (Kabra *et al.*, 2004).

$$hv + \text{semiconductor} \rightarrow h^+ + e^-$$

An electron hole pair is required for initiating a redox reaction although life span of this pair is very short (Bussi *et al.*, 2002). The reaction can continue in different behavior depending on the process of photoreaction. Hydroxyl radicals produce a whole in the valance band that can make a combination with water which begins the chain reaction resultant in oxidation of organic contaminants or it can come together with electrons of the donor group (Kabra *et al.*, 2004). In a parallel way, electron in transmission band can approach together with metal ion whose redox potential is more positive then band gap of photocatalyst or it can join with electron acceptor such as an oxygen molecules form to a superoxide radical (Linsebigler *et al.*, 1995).

Oxidizing agent is needed in most chemical methods for the removal of dyes. The disinfection by-products generating by these oxidizing agents are harmful to human being. Oxidation power is main cause of choosing an oxidizing agent. The ability of dye to form flocs on application of oxidizing agents is main reason of removal of dye. The effect of ozonation on treated water depends on the toxicity of dyes and it is a successful chemical method for removal of dyes although its half-life is very short (Zhang *et al.*, 2002). Most dyes are resistant to photodegradation but removal of dyes by photocatalysis also highly depends on the operating conditions (Kabra *et al.*, 2004).

2.8 Adsorbents

Adsorption is suggested as the excellent wastewater treatment technique due to its inexpensiveness, universal nature and simplicity of operation. Soluble and insoluble organic pollutants can be removed through adsorption process. The removal ability by this technique can be up to 99.9% (Ali *et al.*, 2012). Adsorption can be used for the removal of a variety of organic contaminants from various polluted water sources due to these facts. Fundamentally, accumulation of a substance at a surface or interface takes place during adsorption. The process occurs at an interface between contaminated water and solid adsorbent in case of water treatment

(Ali *et al.*, 2012). The applicability of adsorption depends upon the physical and chemical properties of adsorbent. An adsorbent is projected to have high adsorption capacity, long life and high selectivity. Furthermore, an adsorbent should be obtainable in profusion at low expenditure (McKay, 1996). Broad ranges of adsorbent are easily available and favorably used for the removal of inorganic and organic pollutants. Activated carbon is mostly use as adsorbent. A huge number of low cost adsorbents such as chitosan, biomass, fly-ash, diatomite, acid activated red mud and industrial waste are feasible for removal of dyes (Crini, 2006; McKay, 1996).

2.8.1 Activated Carbon

Activated carbon is the oldest adsorbent acknowledged and an extensive variety of fresh lignocellulosic materials which is utilized for preparing activated carbon such as coal, peat, wood and various agricultural by-products (Zhong *et al.*, 2012). It has strong adsorption aptitude due to its sufficient pore size distribution, high specific surface area and comparatively high mechanical strength. It has been widely engaged in food processing, air contamination control and wastewater treatment (Mudoga *et al.*, 2008; Guo *et al.*, 2007; Crini, 2006). This adsorbent suggests good flexibility and versatility to transform its chemical and physical properties, thus opening the prospect of preparing materials with modified distinctiveness (Haro *et al.*, 2012). Generally, longer activation time and physical initiation involves higher temperature and as evaluated to biochemical initiation, though, due to the use of chemical agents, AC needs a thorough washing in chemical activation. Despite its productive use in water cleansing but the major obstacle for more prevalent applications of activated carbon is its price (Wei *et al.*, 2011).

Thus, a lot of research has been carried out to find out low price adsorbents especially renewable biomass (Ahmed and Dhedan, 2012; Dutta *et al.*, 2011). Therefore, renewal or recycle of exhausted activated carbons is attractive to reduce operational expenditures and to decrease waste production (Foo and Hameed, 2012).

AC is present in two major types: granular activated carbon (GAC) and powdered activated carbon (PAC). GAC is mostly use for the removal of contaminants from wastewater because granular form is easier going to continuous contacting and there is no need to isolate the carbon from the bulk fluid. On the other hand, separation of adsorbent is essential from fluid after using, so the use of PAC presents some serious problems However, due to small money price, easy availability and slighter interaction period obligation, PAC is used for wastewater treatment (Najm *et al.*, 1991). Two other forms of AC's are available other than PAC and GAC. Activated Carbon Pellet (ACP) and Activated Carbon Fiber (ACF). Coal is generally used to prepare the activated carbon, for this purpose it is powdered and re-agglomerated with appropriate binder and then substantially initiated. These materials are prepared particularly for consumption in vapor applications.

Coal is made up of mineral materials carbonaceous resulting from the breakdown of plants. The sorption characteristics of each specific coal are measured by physical–chemical changes occurring after deposition and the nature of the unique vegetation. El Qada *et al.*, (2008); Tamai *et al.*, (1996) and Banat *et al.*, (2007) used it with success for dye removal. However, coal has a diversity of surface properties and thus various sorption properties since is not a pure material.

2.8.2 Low-Cost Adsorbents

Biomass and other waste materials may also offer renewable and an inexpensive additional source of activated carbon. The industrial waste resources have slight or no financial worth and frequently extant removal difficulties. Therefore, there is a requirement to establish these low-cost by-products. So, their exchange into activated carbon would help to decrease the cost of waste disposal, would add economic value and much significantly offer a possibly low-priced substitute to the current commercial activated carbons. An extensive type of activated carbons has been made from biomass and other wastes are given below in table 2.8

Table.2.9 Biomass and waste used in preparation of Activated Carbon

S. No	Biomass and wastes	References
1	Zeolite	(Yan *et al.*, 2009)
2	Vetiver roots	(Altenor *et al.*, 2009)
3	Hevea brasiliensis seed coat	(Hameed *et al.*, 2008b)
4	Peach stones	(Attia *et al.*, 2008)
5	Bio-plant of Euphorbia rigida	(Hameed *et al.*, 2007a)
6	Rattan sawdust	(Hameed *et al.*, 2007b)
7	Sewage char, Furniture and Tyres	(Saniz-Diaz and Griffiths, 2000 ; Lin and Teng, 2002)
8	Polyvilnyldienefluoride fibers	(Yamashita *et al.*, 2001)
9	Fir wood	(Wu and Tseng, 2004)
10	Date pits	(Banat *et al.*, 2003)
11	Olive-seed waste	(Stavropoulos and Zabaniotou, 2005)
12	Wheat bran	(Ozer and Dursun, 2007)
13	Oil palm fiber	(Tan *et al.*, 2007; Hameed *et al.*, 2008a)

14	Jute fiber	(Senthilkumaar *et al.*, 2005)
15	Almond shell, Walnut shell, Hazelnut shell and Apricot stones	(Aygun and Yenisoy-Karakas, 2003)
16	Sugars	(Legrouri *et al.*, 2005)
17	Coconut shell, Bamboo dust, Groundnut shell, Straw and rice husk	(Kannan and Sundaram, 2001; Hameed *et al.*, 2007a)
18	Oil palm shell	(Tan *et al.*, 2008)
19	Coir pith	(Kavitha and Namasivayam, 2007)
20	Vermiculata plant	(Bestani *et al.*, 2008)
21	Coconut husk	(Tamai *et al.*, 1996; Tan *et al.*, 2008)
22	Corncob	(Seng *et al.*, 2006)
23	Pitch	(Tamai *et al.*, 1996)
24	Durian shell	(Chandra *et al.*, 2007)
25	Waste apricot	(Basar, 2006)
26	Rosa canina seeds	(Gurses *et al.*, 2006)
27	Olive stones	(Alaya *et al.*, 1999)

Chapter 3

Materials and Methods

3.1 Experimental Methodology

Within the framework of the objectives laid down for the present study, the focal point was to detect the presence of dyes and its removal from tannery wastewater arising from leather industry effluents. The experimental methodology in this area therefore included the dimension of physicochemical limitations and dyes contents levels using proper standard investigative processes.

3.1.1 Sample Treatment and Analysis

Most of the samples are prepared for analysis but some samples can be measured directly. Various type of sample treatment techniques are used but it depends upon the sample type, analysis for determination and type of method for analysis. Representative sample treatment approaches include solvent extraction and filtration dissolution/digestion etc.

When samples are in effluent form than the parameters measured at the spot has no need of any treatment (Salbu *et. al.*, 1988). However, the excessive particulate matter needs to be filtered off to evade clogging of the target system on the equipment while on the other occasions when dyes content needs to be assessed; sometimes stabilizers are required. Effluents containing colours or the prepared analytic solutions have no problem in measurement.

The exact method for the analysis of sample depends upon the number of samples to be analyzed and expected concentration of analyte present in the sample. For the present study, the analysis of physico-chemical parameters and the removal of dyes content were termed and debated with respect to their implication and technical guidelines adapted to this effect.

3.1.2 Sampling Plan

The sampling plan for this work was carefully prepared with consultation and collaboration of practical staff of Environmental Analytical Laboratory (EAL) Islamabad. It was decided that 10 sites would be specified and 5 samples would be collected from each site from variable distances.

The study included the measurement of physico-chemical parameters such as temperature, pH, sulphate, Phosphate, Sodium, conductivity, alkalinity, chloride, calcium and potassium.

The basic plan of sampling was to gather samples to confirm better quality valuation during the analysis. All samples were analyzed at the Environmental Analytical Laboratory (EAL), Pakistan Council of Scientific and Industrial Research (PCSIR).

3.1.3 Description of Sampling Site

Kasur is a famous industrial city in the central Punjab, Pakistan which contain 2.5 million population over area of 3995 Sq.Km. Most land of Kasur is plain fields. It is irrigated with the water of Indus River and groundwater is also drawn with the help of tube-wells. Kasur is feeding more than 7 million people of the region because wheat, rice, sugarcane and cotton are rich cash-crops of this area. The city has very old industrial setup and houses a large number of small and big industrial units of which the tanning units are the most leading. Other industries in the city include glazed pottery, textile, Sugar, woodworks and embroidery.

3.1.4 Sampling of Tannery Effluents

For identification and detection of dyes and physico-chemical parameter determination in tannery effluent, various tanneries located in Kasur, was selected. A total of 50 samples were collected from 10 different sites of tannery area. From each site, 5 samples were collected from different distances. Every sample bottle was labeled properly and directly transported to the lab for compulsory analysis.

The tannery effluent samples were collected in polythene bottles of 1.5 litter capacity. These bottles were sweep away thoroughly with 5 % detergent solution, 1:1 $FINO_3$, tap water and lastly with distilled water. The temperature of samples was measured at the sampling site but other parameters were measured in lab. The samples were examined in harmony with the standard methods. All related evidence about the samples was accordingly noted down at the sampling time.

3.1.5 The Glassware Volumetric Apparatus

The sample treating for precise analysis needs appropriate glassware and volumetric contraption which is not vulnerable to the leaking consequence of generally used robust oxidizing agents, acids and bases for the solution making and sample digestion. Consequently, all glassware used during the current study was of high excellence, acid resilient borosilicate pyrex glass. The glassware was first given a full washing with chromic acid and then with 5 % (w/v) detergent solution in order to evade impurities. Later, it was cleaned with 10 % (v/v) HNO_3 and lastly with purified water. In cases where some organic matter was supposed to pollute an assumed piece of glassware, it was finally washed with acetone. The glassware was then put in an electric oven at 60°C (±1°C) for about six hours previous to use. All volumetric tools used for dispensation of samples, dilution or making up volumes of the solutions was preserved the same way.

3.2 Determination of Physico-chemical Parameters

3.2.1 Temperature

Temperature analyses were used in the measurement of several form of alkalinity, in study situation and constancy related with calcium carbonate, in the measurement of salinity and in common laboratory maneuvers.

Procedure

Temperature of all samples was measured at the sampling sites. For this purpose, a high quality mercury filled Celsius thermometer was used. After collecting sample in bottle, thermometer was dipped in the sample and after passing some time, it was carried out and reading was noted.

3.2.2 pH

pH is one of the most significant water excellence indices. This disturbs the chemical and biological processes happening in natural waters. The fluctuations in water pH are closely associated to the decay of the organic matter. Furthermore the speciation of lethal metals is significantly inclined by pH. Many industrial wastewaters enclose mineral acids. The wastewater from leather industry holds sulphide which is changed to sulphuric acid and sulphates by sulphur oxidizing bacteria at precise pH. It is batter that pH should be measured after collection of sample. The pH was measured by using the electrochemical method whereby a pH electrode standardized with solutions of pH 4 and 7 was absorbed in the water sample and the measurement was made.

Procedure

A portable, dual powered pH meter, HANNA Membrane pH meter, model HI 8314 was used to measure the pH of all samples. It was pre-rectified by using standard buffer solutions of pH 4.0, 7.0 and 9.0. The samples were taken in glass beakers one by one to measure the pH. After each measurement, the electrode of the pH meter was washed with distilled water and cleaned with a piece of tissue paper.

3.2.3 Electrical Conductivity

Electrical conductivity is used as an estimated measure of the whole concentration of inorganic substances in water. The main ions impelling conductivity are H^+, Mg^{2+}, Ca^{2+}, Cl^-, Na^+, K^+, BO_4^{2-}, and HCO_3^{2-}, other ions such as Mn^{2+} Al^{3+}, Fe^{2+}, Fe^{3+}, HPO_4^{2-} etc. and dissolved gases have only a minor effect on conductivity.

Reagents

(a) Conductivity water: Any of several methods can be used to prepare reagent grade water.

(b) Standard potassium chloride solution, KCL, 0.0100M: Dissolved 745.6 mg anhydrous KCL in conductivity water and dilute to 1000 mL in a volumetric flask.

Procedure

Conductivity cell was washed with at least three portion of 0.0100M KCL solution. Conductivity meters often indicate conductivity directly. Now cell of electrode was thoroughly rinsed with one or more portion of sample. 1 mL sample was diluted in 100 mL distilled water. This sample was taken in a flask and cell of conductivity meter was dipped in sample. After that conductivity was noted down with temperature. Cell was clean with distilled water after measuring every sample.

3.2.4 Total Dissolved Solid (TDS)

Solids state to substance deferred or liquefied in water or wastewater. Solids may disturb water or effluent worth harmfully in a number of ways. Water with most liquefied solids normally is of substandard delectableness. For these reasons a perimeter of 500 mg dissolved solids/L is desirable for drinking water. Total Dissolved Solids is a quantity of the collective residues of all inorganic and organic materials present in a liquid in: ionized, micro-granular suspended or molecular form.

Procedure

TDS was measured at conductivity meter. The cell of conductivity meter was rinsed with distilled water and gently clean and dry with tissue. Then 1 mL sample was taken and it was diluted in 100 mL of distilled water. This volume was made in a volumetric flask. The cell was put into the flask to measure total dissolved solids. When reading with temperature became constant then it was noted. Cell was clean with distilled water after measuring every sample.

3.2.5 Chloride

Chloride, in form of chloride (Cl^-) ion, is one of the major inorganic anion in water and wastewater. The salty taste produced by chloride concentration was variable and dependent on chemical composition of water. Its concentration in water supplies is limited to 250 mg/L by WHO as at higher concentration. Higher chloride concentration is also harmful for plants. Chloride is commonly estimated by three methods which are Mercuric nitrate method, potentiometric method and Argentometric method.

Reagents

The argentometric method was used for the determination of chloride in three media. The reagents required for this method include

(a) Potassium chromate indicator solution: 50 g of K_2CrO_4 was dissolved in approximately in 100 ml distilled water. The $AgNO_3$ (aq) solution was added, until a definite red precipitate was formed. This solution was allowed to stand for 12 hours, filtered and diluted to 1 L with distilled water.

(b) Standard silver Nitrate titrant 0.0141 M: standardization of 0.014M $AgNO_3$ was carried out against standard NaCl (aq)

(c) Standard sodium chloride 0.0141: for this solution 824 mg NaCl was dissolved in small amount of distilled water and diluted to 1 L.

Procedure:

An aliquot of 1 mL of sample was diluted to 100 ml and from this diluted sample, 25 ml sample was taken in flask. 1 mL of K_2CrO_4 indicator solution was added in sample then the sample color became yellow. After that this sample was titrate with standard $AgNO_3$ titrant to pinkish yellow end point. The chloride contents were determined in term of mg/L by using following equation.

mg/L Cl^- = (A x M x 35450) / mL of sample

A = mL titrant used

M= morality of $AgNO_3$ slandered solution

3.2.6 Calcium

Calcium is a chemical element and its atomic number is 20 with symbol Ca. It is a fifth-most-copious component by quantity and soft gray alkaline earth metal in the Earth's crust. Calcium is significant for prevailing entities, specifically in cell physiology, where movement of the calcium ion Ca^{2+} takes place into and out of the cytoplasm functions as a signal for many cellular progressions. Calcium is the richest metallic by quantity in many animals as a major material used in mineralization of bone, teeth and shells

Reagents

(a) Sodium hydroxide, NaOH, 1N

(b) Murexide (Indicator). This indicator was prepared by dissolving 150 dyes in 100 g absolute ethylene glycol.

(c) Standard EDTA titrant, 0.01 M. 3.723 g of analytical reagent grade disodium ethylenediaminetetraacetate dehydrate and was dissolved in distilled water and diluted to 1000 mL.

Procedure

1 mL sample of tannery wastewater was taken and it was diluted in 100 mL distilled water. Then 25 mL sample was taken in a flask. Some drops of indicator were added in this sample. After that, it was titrant with EDTA. EDTA was added slowly with continuous stirring to the proper end point. The colour was changed from pink to purple at end point.

Calculation

mg Ca/L = EDTA used x 0.405 x 1000 / Sample Volume

3.2.7 Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is one of the most appropriate chemical parameters for the controlling of wastewater behavior accommodations with the control of the worth of a waste. Chemical oxygen demand (COD) is the key guide used to measure organic contamination in aqueous systems. COD can be defined as the number of oxygen is equaled to use up in the oxidation of organic composites via powerful oxidizing agents such as permanganate and dichromate. Consequently, the normally used method for the detection of COD is titrimetry using $FeSO_4$ as the titrant. The value of COD shows the oxygen equivalent of the organic contented that may be oxidized by potassium dichromate ($K_2Cr_2O_7$) consuming silver sulfate (Ag_2SO_4) as a catalyst under acidic conditions (H_2SO_4).

Reagents

(a) Sulfuric acid containing silver: 15 g silver sulfate was dissolved in 1 L concentrated sulfuric acid.

(b) Potassium dichromate solution: 12.259 g of potassium dichromate (dried for 2 hours at 105 °C) was taken and dissolved in 1 L of distilled water. 100 mL of this solution was made up to 1 L with water.

(c) Ferrous ammonium sulfate solution: 98 g ferrous ammonium sulfate was dissolved in distilled water. 20 mL of concentrated sulfuric acid were added and solution made up to 1 L with water. 100 ml of this solution was made up to 1 L with water.

(d) Ferroin indicator: 0.98 g ferrous ammonium sulfate and 1.485 g 1:10 phenanthroline was taken and dissolved in water and made up to 100 mL of solution.

Procedure

Before measuring COD, factor adjustment of ferrous ammonium was carried out. For this purpose 10 mL of more concentrated potassium dichromate solution was diluted to 100 mL. 30 ml more concentrated sulfuric acid was added, the solution was cooled and titrated with ferrous ammonium sulfate after adding 3 drops of ferroin indicator. The amount x consumed (mL) was used to calculate the factor according to $f = 10/x$ which was checked daily.

The determination was carried out as followed. 1 mL of sample was diluted to 20 mL and 10 mL of more concentrated potassium dichromate solution placed into the flask with anti-bump granules. Afterwards 30 mL of silver containing sulfuric acid was carefully added with shaking. The solution was then carefully boiled at 150 °C under reflex for 2 hours. After heating, the solution cooled and condenser was rinsed with distilled water until the volume of solution was about 150 mL. After cooling at room temperature, 3 drop of ferroin indicator was added then the excess of dichromate was back titrated with the ferrous ammonium sulfate. The color was changed from blue green to red brown color at the end point. A control sample consisting of 20 mL distilled was measured at same time.

Calculation of result

The COD value was given in mg/LO_2

COD (mg/L) = (a-b).f.2000 mg/V

a= Ferrous ammonium sulfate consumed by blank (mL)

b= Ferrous ammonium sulfate consumed by sample (mL)

f= titration factor of Ferrous ammonium sulfate solution (mL)

V= sample volume (mL)

3.2.8 Sulphate

Sulphate (SO_4^{2-}) is widely dispersed in nature and may be current in natural water in concentration in ranging from a few to numerous thousand milligrams per liter. Mine drainage water may contribute large amount of SO_4^{2-} through pyrite oxidation. Sodium and magnesium sulfate exerts a cathartic action.

Reagents

(a) Buffer Solution A: Dissolved 30 g magnesium chloride, $MgCl_2.6H_2O$, 5 g sodium acetate, $CH_3COONa.3H_2O$, 1.0 g potassium nitrate, KHO_3, 20 ml of acetic acid, CH_3COOH (99%) in 500 mL distilled water and make up to 1000 mL.

(b) Barium Chloride, $BaCl_2$, crystals, 20-30 mesh. In standardization, uniform turbidity was produced with this mesh, range and appropriate buffer.

(c) Standard Sulfate Solution: prepare standard sulfate solution to dilute 10.4 mL standard 0.0200 N H_2SO_4 titrant Alkalinity to 100 mL with distilled water.

Procedure

1 mL of sample was taken and it was diluted in 100 mL of distilled water. Then 48 mL of this diluted sample was taken in volumetric flask of 50 mL. After that 2 mL of buffer solution A was added and mixed properly. Then added a spoonful of $BaCl_2$ crystals and begin timing immediately. Shake it well to mix.

After that, the level of phosphate was measured at UV spectrophotometer at range of 420 nm. Standard was taken in on cuvett and sample in other. Then both standard and sample was put in spectrophotometer and reading was taken. Reliability of calibration curve was checked by running standard with every 3 or 4 samples.

Calculation

$mg(SO_4^{2-})/L = mg\ (SO_4^{2-}) \times 1000/\ mL\ sample$

3.2.9 Nitrate

Nitrate (NO_3^-) is an essential source of nitrogen for plant and animal life and it is composed of the elements oxygen and nitrogen. Too much nitrate in drinking water can be dangerous to human condition. Synthetic or man generated causes of nitrogen overview into the subsurface surroundings consist of poisoned tank systems, animal waste removal and agricultural fertilizers. Methaemoglobinaemia can be caused by nitrates in newborns, augmented nitrate absorptions in groundwater have controlled to the closure of wells and reduced aquifers useless as water sources.

Reagents

(a) Nitrate free water: Used redistilled or distilled demonized water of highest purity to prepare all solution and dilutions.

(b) Stock nitrate solution: Dried potassium nitrate (KMO_3) in an oven at 105 °C for 24 hours. Dissolved 0.7218 g in water and dilute to 1000 mL; 1.0 mL = 100 µg NO_3^- -N. preserve with 2 mL $CHCl_3$/L.

(c) Standard nitrate solution: Diluted 1.0, 10 and 50 mL stock solution to 100 mL with water to obtained standard solutions of 1.0, 10 and 50 mL NO_3^- -N.

(d) Buffer solution: Dissolved 17.32 g $Al_2(SO_4)3.18H_2O$, 3.43 g Ag_2SO_4, 1:28 g H_3BO_3 and 2.52 g sulfamic acid (N_2NSO_3) in about 800 mL water.

(e) Sodium Hydroxide, NaOH, 0.1 N

Procedure

Transfer 1 mL of 1 mg NO_3^- -N/L standard to a 50 mL beaker, add 10 mL buffer and stir with a magnetic stirrer. Immerse tips of electrodes and recorded milivolt reading when stabled. Remove electrode, rinse and blot dry. It was repeated 10 mg NO_3^- -N/L standard. 10 mL sample was transferred to a 50 mL beaker and 10 mL solution was added then it was stir for 1 minute with a magnetic stirrer. Standards and samples were measured at about same temperature, Tip of electrode was immersed in sample and potential reading was note down when it stabled.

3.2.10 Nitric Acid Digestion for Analysis of Heavy Metals

To reduce interference by organic matter and to convert metals associated with particulate to a form (usually the free metal) that can be determined by atomic absorption spectrometry. Nitric acid digests most samples adequately. Nitrate is an acceptable matrix for both flame and electrothermal atomic absorption. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized material. Acid digestion techniques generally yield comparable precision and bias for most samples type that are totally digested by the technique.

(a) Apparatus

(1) Hot plate

(2) Griffen beakers, 150 mL

(3) Volumetric flasks, 50 mL

(4) Watch glasses, ribbed and unribbed

(b) Reagent

Nitric acid, HNO_3, concentrated, analytical or trace metal grade

Procedure

10 mL sample of tannery effluent was taken in a beaker and 5 mL of concentrated nitic acid was added and then well mixed. After that, hot plate was run and samples were place on the hot plate. These samples were boiled for 90 minutes at 150 °C. When the sample started to boil and its volume remained very low before precipitation then samples was took up from the hot plate and left them to cool. Add more conc. HNO_3 if it is necessary until digestion was completed. Do not let sample dry during digestion.

After digestion sample and cool it down, the samples was filtered with Whatman 42 filter paper in a volumetric flask of 50 mL. The volume of sample was made up of 50 mL by adding distilled water.

3.2.11 Metal Analysis by Atomic Absorption Spectrophotometer (AAS)

Vario 6 AAS was used to determine the selected essential and non-essential metals. With complex matrix, AAS vario 6 was entirely programmed atomic absorption spectrometer for ultratrace analysis of real-world samples. For the analytical capabilities of the total system, it contained transverse heating of the graphite furnace which was a critical requirement for efficiency. This arrangement delivered exceptional analytical presentation in terms of detection, reproducibility and precision. The transversely heated furnace system with autonomously manageable gas flowed to ensure outstanding analytical situations due to almost perfect temperature conditions, long periods of graphite tubes and furnace substantial. Its Fast Furnace Concept confirmed very short examination times. It covered different tube and platform types for optimum variation to all types of analytical responsibilities from simple to multifaceted analyses.

3.2.12 Quantification of AAS Results

The standard adjustment method was implemented for quantification of results. Standard solutions were ready in proper range (10-100 ppm) and their absorptions were noted on the instrument. The instrument in programmed mode plots the calibration line itself. At least five standards were run covering the absorption range of samples. The working graph was observed infrequently by making measurements with the standard solutions. New standard line was drawn every time earlier running the samples on AAS system. The blanks ready under same analytical situations but deprived of the sample were regularly used to estimation the related reagent metal levels. Standard orientation material was used to check the exactness of the results and the accuracy of the instrument.

3.3 Removal of Dye by Adsorption

3.3.1 Analysis of Dyes

A dyeing wastewater collected from a leather dyeing factories in Kasur and used to evaluate the effectiveness of the activated carbon in the treatment of wastewater. Coloured samples of tannery effluents were scanned by UV-visible spectrophotometer. Acid blue 193 dye was detected and selected for present study. For this purpose, the dye was obtained from a tanning unit. The synthetic wastewater of Acid blue 193 was ready by liquefying dyestuffs in distilled water to prepare a stock solution of 1 g/L. Different concentrations were prepared by distilled water from this stock solution for batch study. The UV–visible spectrum of each dye solution was before measured and acknowledged the extreme absorption wavelength (λ max).

3.3.2 Activated Carbon

Activated carbon was the most extensively used adsorbent for wastewater management and water contamination regulator. Activated carbon was used in this study as adsorbent. This activated carbon was prepared from coal and purchased from the market.

3.3.3 Adsorption Studies

Adsorption study was undertaken to study the effects of dose of activated carbon, initial solution pH, adsorption time, initial dye concentration and adsorption temperature.

3.3.4 Effect of dose of Activated Carbon

To find out the effect of adsorbent on dye removal, different concentrations of activated carbon was used. The doses were 0.1 g, 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g, 3.0 g and 3.5 g respectively. The volume of each sample was 50 mL. After preparing the samples, these were placed into the shaking water bath at 30 °C at 120 rpm. The shaking duration of each sample was 4 hours. After the 4 hours, samples were placed outside till settlement of AC. Once the equilibrium was established, supernatant liquid was filtered off using Whatmann filter paper No. 42 and uptake of the dye was determined by using UV-visible spectrophotometer. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase.

3.3.5 Effect of pH

To find out the effect of pH on dye removal, different samples were prepared having pH rang of 3-9 respectively. The volume of each sample was 50 mL. Amount of adsorbent was 2.0 g for each sample. After preparing the sample, these were placed into the shaking water bath at 30 °C at 120 rpm. The shaking duration of each sample was 4 hours. After the 4 hours, samples were placed outside till settlement of adsorbent. Once the equilibrium was established, supernatant liquid was filtered off using Whatmann filter paper No. 42 and uptake of the dye was determined by using UV-visible spectrophotometer. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase.

3.3.5 Effect of Initial dye concentration

To find out the effect of initial dye concentration on dye removal, different concentrations of dye was used. The dye concentrations were 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L, and 350 mg/L respectively. Amount of adsorbent was 2.0 g for each sample. The volume of each sample was 50 mL. After preparing the samples, these were placed into the shaking water bath at 30 °C at 120 rpm. The shaking duration of each sample was 4 hours. After the 4 hours, samples were placed outside till settlement of AC. Once the equilibrium was established, supernatant liquid was filtered off using Whatmann filter paper No. 42 and uptake of the dye was determined by using UV-visible spectrophotometer. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase.

3.3.5 Effect of Temperature

To find out the effect of temperature on dye removal, sample was prepared. Amount of adsorbent was 2.0 g for each sample. The volume of each sample was 50 mL. After preparing the samples, these were placed into the shaking water bath at 120 rpm. The temperature of water bath set as 30 °C, 32.2 °C, 40 °C, 45 °C and 50 °C. The shaking duration of sample was 4 hours. After the 4 hours, samples were placed outside till settlement of AC. Once the equilibrium was established, supernatant liquid was filtered off using Whatmann filter paper No. 42 and uptake of the dye was determined by using UV-visible spectrophotometer. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase.

3.3.6 Effect of Contact Time

To find out the effect of time duration of shaking on dye removal, sample was prepared. Amount of adsorbent was 2.0 g for each sample. The volume of each sample was 50 mL. After preparing the samples, these were placed into the shaking water bath at 30 °C at 120 rpm. The shaking time of samples was 30, 60, 90, 120, 150, 175 and 200 minutes respectively. After that, samples were put outside till settlement of AC. Once the equilibrium was established, supernatant liquid was filtered off using Whatmann filter paper No. 42 and uptake of the dye was determined by using UV-visible spectrophotometer. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase.

3.3.7 Removal Percentage

The removal percentage, defined as the ratio of difference in initial dye concentration before and after adsorption ($C_i - C_e$) to the initial dye concentration in the aqueous solution (C_i), was calculated using the following equation (Hameed *et al.*, 2007b):

$$\% \, Removal = \frac{Ci - C_e}{Ci} \; x \; 100$$

Where

C_i = initial concentration of dye

C_e = final concentration of dye

3.3.8 Statistical Analysis

The elementary statistical parameters included standard deviation, standard error, minimum, maximum, mean, media and kurtosis, essential to determine the extent and circulation of measured data. For this purpose, origin 7.5 was used as statistical tool.

Chapter 4

Results

4.1 Layout of Data

The generated data during this study was presented in form of tables and graphs. Overall mean values of metal contents and physicochemical parameters were shown in tables while removal of dye contents and mean concentration of metal from every site was presented in graphical form.

4.1.1 Effect of dose of adsorbent

Effect of dose of adsorbent was study during this investigation. Different concentration of adsorbent was used. The range of adsorbent was 0.1-3.5 g/100 mL. It was seen that as the concentration of adsorbent was increasing, the removal of dye was also increasing. At minimum concentration of adsorbent which was 0.1 mg/100 mL, the removal was 16.3%. When the dose of adsorbent was increased to 3 g/100 mL, the removal of dye was 81.9% which was maximum removal. It increased from 16.3% to 81.9%. But after that, when the dose was 3.5 g/100 mL, it was observed that removal of dye was 76.6%. It showed that after a specific amount of adsorbent, the removal was starting to decrease.

4.1.2 Effect of solution pH

pH of solution has an important effect on adsorption of dye because it defines speciation of the adsorbate, the degree of ionization and the charge of the adsorbent surface. In this study, removal of dye was also measured by varying the pH of the dye solution. Study was carried out at pH range of 3-9. It was found that removal percentage was more at acidic pH compared with removal at basic pH. The removal of dye was maximum at pH of 5 and 6. At pH of 5, removal was 84.1% and at pH of 6, it was 87.2%. It was also observed that as the medium was becoming basic, the removal of dye was decreasing because dye adsorption was found minimum at pH of 9 which was 63.8%. Removal of dye was observed maximum during the acidic pH but it was decreasing during basic pH.

Generally, adsorption characteristics on activated carbons in liquid phase depend on pH because the surface charge changes with pH. The surface functional groups contribute to the surface charge. According to the electrostatic mechanism, the theoretical maximum removal percentages of acid dyes should appear in range pH 6–8, while the experimental value was in pH range of 5–6. This phenomenon suggested that the electrostatic interaction was not the sole mechanism of adsorption. In fact, the spatial structures of dye molecular may influence this adsorption process, which is needed to be studied further.

4.1.3 Effect of initial dye concentration

The adsorption study was carried out in initial study concentration of 50 mg/L-350 mg/L. It was observed that at lower concentration, the removal of dyes was found maximum and reached at 82.5 % but removal was 42.7% within increasing the dye concentration. It was showing that as the concentration of dye was increasing, the percent removal was decreasing. Dye removal efficiency was higher for low initial concentration because of availability of unoccupied binding sites on the adsorbents. Percent color removal decreased with increasing dye concentration because of nearly complete coverage of the binding sites at high dye concentration. The consequence of early dye concentration on dye adsorption could be endorsed to the rise in the driving force of the concentration incline with an increase in the primary dye absorption (Chiou and Li, 2002).

4.1.4 Effect of Temperature

The adsorption study was also performed with parameter of temperature. The temperature range of water bath shaker was set from 30 °C - 50 °C respectively. It was found that when temperature was 30 °C, the adsorption of dye was 77.4%. The removal was increasing with increased temperature. At the temperature of 32.5 °C, 91.7% dye was removed. But as soon as temperature was established at 40 °C and 45 °C, the removal of dyes was decreased as 84.2% and 81.6%. But when temperature was 50 °C, maximum 93.8% removal was found. It showed that the rate of dye removal was maximum at temperature of 32.5 °C and 50 °C. The rate of uptake of dye with AC increased with increase in temperature for AC, thereby indicating process to be endothermic in nature. It is apparent that the maximum adsorption for AC occurred at 50 °C.

4.1.5 Effect of contact time

The result of interaction time for the adsorption of dye was studied. The period of study was 30-200 minutes for initial dye concentration of 100 mg/L at relevant optimum pH. The absorption of dye was very low at first 30 minutes. But it was seen that as increasing the time period, the percent of dye absorption was increasing. The absorption of dye was found maximum at the contact time of 200 minutes. The removal percentage at this time was 86.7. The experiment showed that adsorption also depends upon the contact of time of adsorbent with dye.

4.2 Determination of Physico-chemical Parameter from Tannery Effluents

Tannery wastewater was having alkaline and acidic liquors with highly colour and unpleasant smell in liquid (World Bank, 1999). The recorded effluent temperature diverse between 25.8 and 34.4°C, with a mean value of 30.17 °C, falling close to the ambient temperature prevailing during effluent sampling. The temperature of an effluent body has a number of indirect effects on water bodies admixing with the effluent. The temperature changes cause changes in the solubility of oxygen gas in water thus affecting living organisms. A change in temperature also influences the metabolic rates and solubility of various trace metal ions dispersed in water through effluents (UNEP, 1991).

The tannery effluent showed variation in pH running from 3.18 to 9.39. This observed pH variation was an outcome of acidic and basic chemicals used during leather tanning and processing stages. Normally, tanning is carried out at relatively high pH of bath solutions to ensure chromium deposition in the skin structure (Dasgupta, 1998). Electrical conductivity was measured to detect the solubilized ionic species in the effluents, ranged from 3.36 mS/cm to 197.9 mS/cm, with 51.35mS/cm as the mean value. The high values reflected high ionic load while low conductance values related to a low ionic load in effluents. TDS was also measured during this study. The range of TDS was found 1650mg/L to 95900 mg/L with mean value of 21815.2 mg/L.

Chloride is an important part of tannery wastewater. It was found in range of 985mg/L to 28580 mg/L with mean value of 6775.72 mg/L. The high chloride content of the effluent was measured to stem mostly from the usage of sodium chloride in the pre-treatment stages of tanning. The present range of chloride concentration exceeds the permissible levels of chlorides for safe effluent discharge (Bosnic *et al.*, 2000).

Sulphate is a significant constituent present in tannery wastewater. Sulphate was also measured during this study. The range value of sulphate was 299.9 mg/L to 15079.5 mg/L while the mean value was 3924.88 mg/L. It clearly showed that sulphuric acid or produces with high (sodium) sulphate content with several supplementary chemicals was used during the tanning process.

When the nitrate was measured, the range of it was 297 mg/L to 5910 mg/L with mean range of 1774.08 mg/L. It showed that proteinacious materials during liming or unhairing operation and ammonia during from deliming process was used. Calcium was also measured as an important parameter of tannery effluents. The range of calcium was found 486 mg/L to 14904 mg/L, with 3719.48 mg/L as the mean value.

Chemical oxygen demand (COD) is known as most important parameter of tannery wastewater. COD was measured to find out the level of organic pollutants present in wastewater. COD was also measured during this study and the range of COD was 198 mg/L O_2 to 5742 mg/L O_2 respectively. The mean range of COD was 1804.88 mg/L O_2. It showed that oxygen compulsory to oxidize the effluent samples was exclusively present in the tannery effluent.

4.2.1 Metal Distribution

Various metals like Cr, Cd, Zn, Ni, and Pb were measured during present study. Chromium with a mean concentration was found of 412.57 mg/L. The mean concentration levels of Cd, 6.93mg/L, Zn 8.53 mg/L, Ni, 9.52 mg/L and Pb, 11.59 mg/L respectively. Mean value of these metals from each site was also measured. The composite level of these metals from site one was Cr, 223.88 mg/L, Cd, 4.72 mg/L, Zn, 5.58 mg/L, Ni, 6.42 mg/L and Pb, 7.82 mg/ L. Mean level of these metals from site two was Cr, 251.76 mg/L, Cd, 6.02 mg/L, Zn, 7.04 mg/L, Ni, 7.06 mg/L and Pb, 8.24 mg/L. From site three, the mean values of these metals were Cr, 106.76 mg/L, Cd, 3.74 mg/L, Zn, 4.22 mg/L, Ni, 4.78 mg/L and Pb, 6.62 mg/L. Composite level of these metals from site four were Cr, 365.78 mg/L, Cd, 6.98 mg/L Zn, 8.3 mg/L Ni, 8.72 mg/L and 10.36 Pb, mg/L. From site five, mean concentration of these metals were Cr, 401.6 mg/L, Cd, 7.8 mg/L Zn, 8.84 mg/L Ni, 9.72 mg/L and Pb, 11.0 mg/L. Composite level of these metals from site six were Cr, 338.96 mg/L, Cd, 6.74 mg/L Zn, 7.2 mg/L Ni, 8.28 mg/L and Pb, 9.92 mg/L. At site seven, it was Cr, 939.96 mg/L, Cd, 11.2 mg/L Zn, 14.1 mg/L Ni, 16.8 mg/L and Pb, 21.68 mg/L. Mean concentration of these metals from site eight were Cr, 786.58 mg/L, Cd, 10.2 mg/L, Zn, 13.88 mg/L, Ni, 15.36 mg/L and Pb, 18.2 mg/L. At site nine, composite level was Cr, 213.82 mg/L, Cd, 5.16 mg/L Zn, 6.68 mg/L Ni, 8.28 mg/L and Pb, 9.8 mg/L. Composite level of these metals from site ten was Cr, 492.86 mg/L, Cd, 6.78 mg/L Zn,9.46 mg/L Ni, 9.86 mg/L and Pb, 12.34 mg/L respectively.

Mean of total samples (n=50) and mean of every metal from each site showed that the level of each metal was extremely high. The level of these metals was surpassing high from the levels proposed by National Environmental Quality Standards for the safe discharge of effluents.

TABELS

Table 4.1 Basic statistics for physico-chemical parameters of tannery effluents (n=50)

	Temperature °C	pH	Total Dissolved Solid (mg/L)	Conductivity (mS/L)
Minimum	25.8	3.18	1650	3.36
Maximum	34.4	9.39	95900	197.9
Range	8.6	6.21	94250	194.54
Mean	30.17	5.98	21815.2	51.35
Median	30.35	6.81	14030	35.85
SD	1.94	1.96	22928.89	51.87
SE	0.275	0.278	3242.63	7.33
Variance	3.78	3.85	5.25	2690.84
Kurtosis	-0.053	-1.52	3.51	2.34

Table 4.2 Basic statistics for physico-chemical parameters of tannery effluents (n=50)

	Chloride (mg/L)	Nitrate (mg/L)	Calcium (mg/L)	COD (mg/L O_2)	Sulphate (mg/L)
Minimum	985	297	486	198	299.9
Maximum	28580	5910	14904	5742	15079.5
Range	27595	5613	14418	5544	14779.6
Mean	6775.72	1774.08	3719.48	1804.88	3924.88
Median	4631.5	1510	2835	1477	2367.5
SD	6819.49	1241.10	3472.64	1338.55	3613.07
SE	964.42	175.51	491.10	189.29	510.96
Variance	4.65	1.54	1.20	1.79	1.30
Kurtosis	2.93	1.45	3.34	0.158	1.18

Table 4.3 Elementary statistical parameters* for the dissemination of designated metals in tannery effluent samples (n=50)

Metal	Maximum	Minimum	Range	Mean	Median	SD	SE	Kurtosis
Cr	1812	10.4	1801.6	412.57	340.05	391.57	55.41	4.15
Cd	22.6	2.4	20.2	6.93	5.6	4.14	0.58	4.24
Zn	30.7	2.3	28.4	8.53	7.7	5.48	0.77	6.20
Ni	37.8	3.5	35.7	9.52	8.25	6.61	0.93	7.05
Pb	50.9	3.6	46.6	11.59	9.65	8.33	1.17	9.40

*** mg/L where applicable**

FIGURES

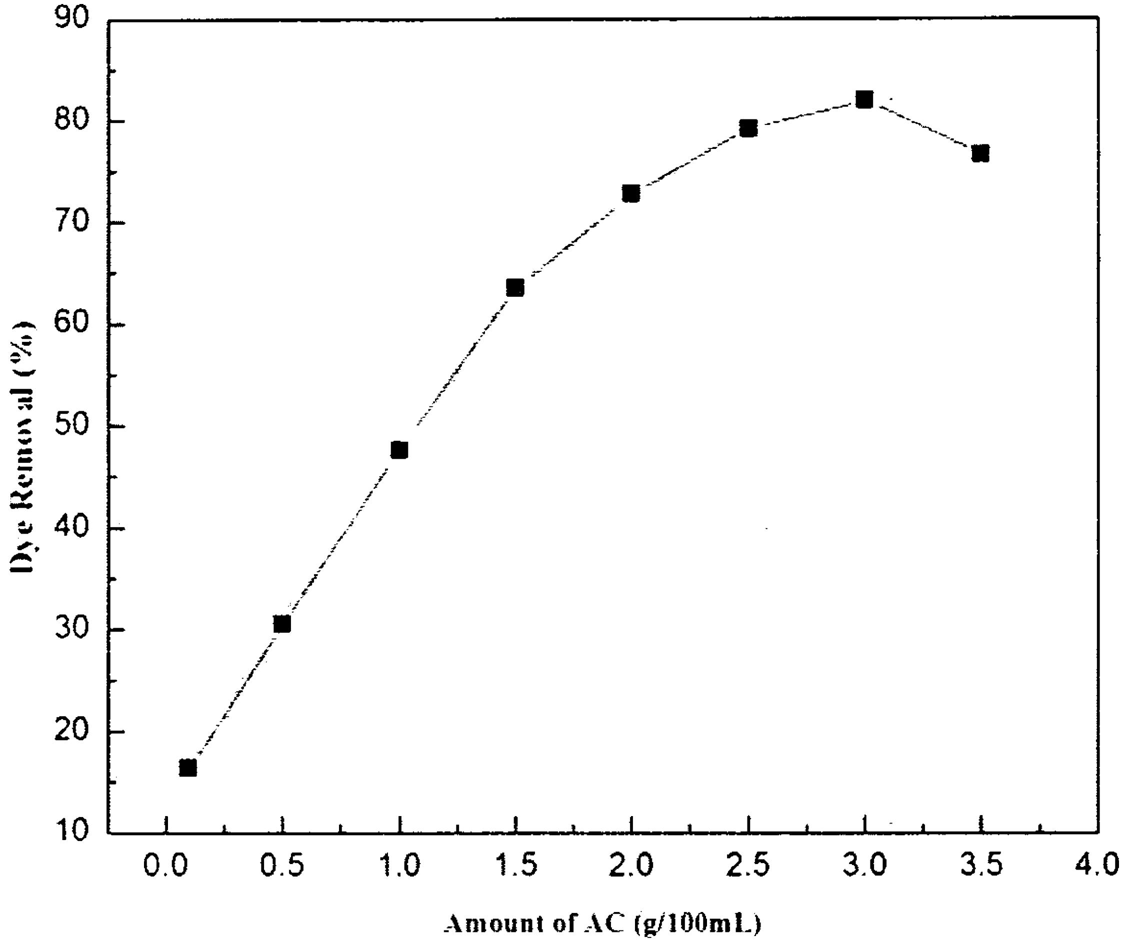

Figure 4.1 Effect of dose of AC on adsorption of dye

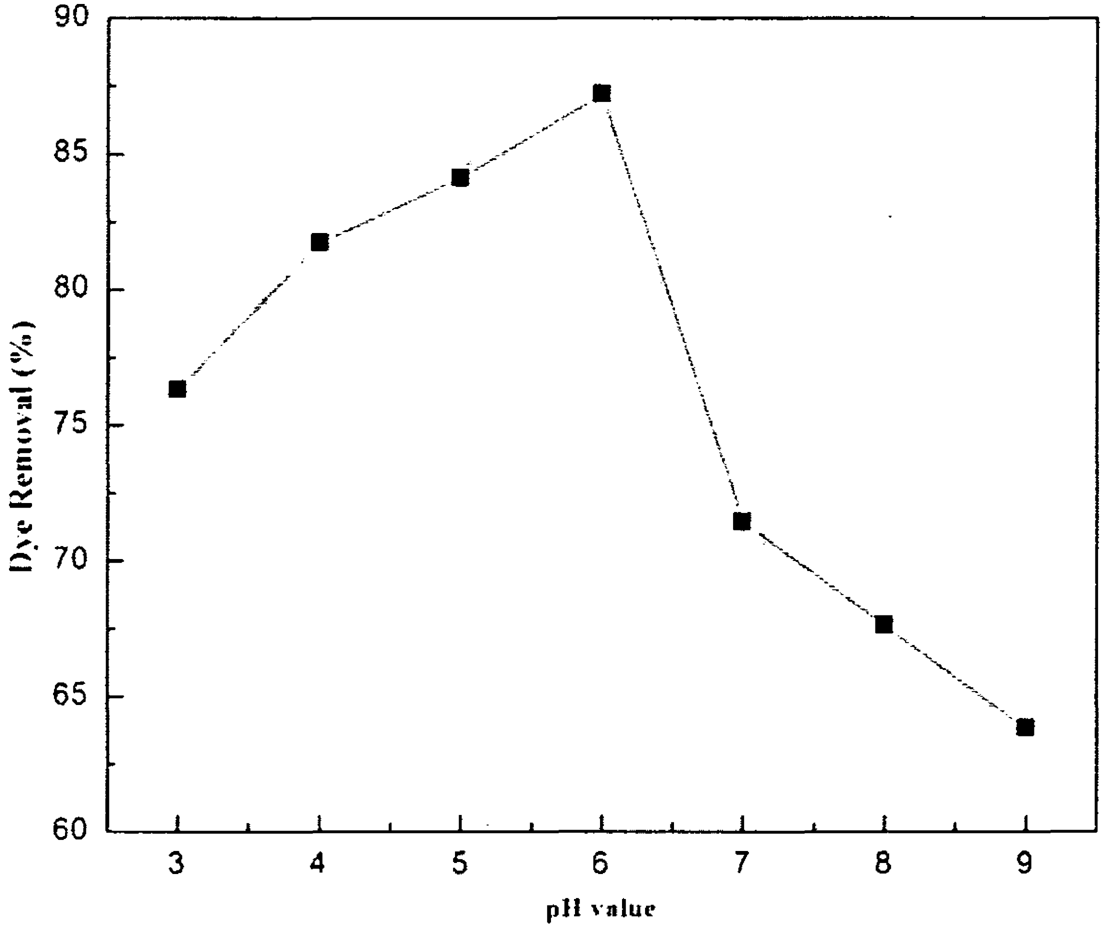

Figure 4.2 Effect of initial pH of solution on dye removal by using AC as adsorbent

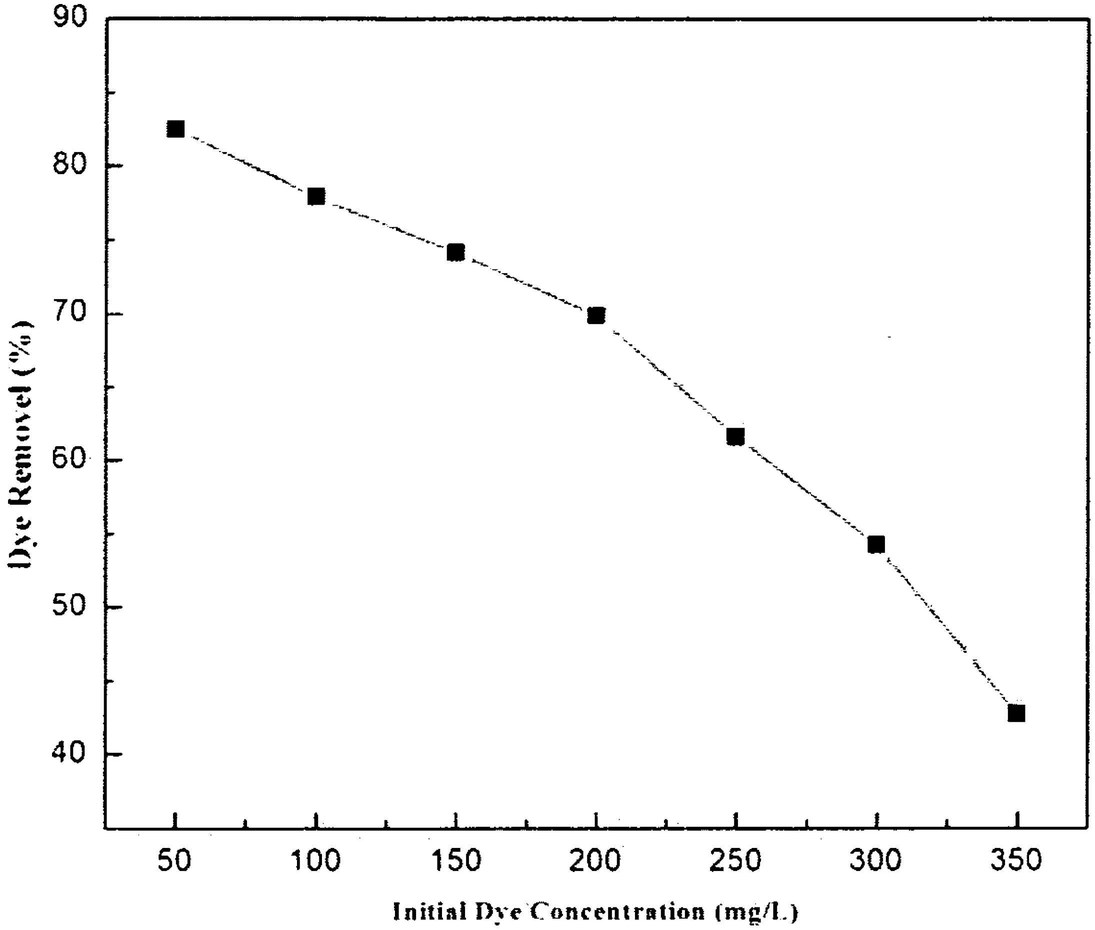

Figure 4.3 Effect of initial dye concentration on dye removal by using AC as adsorbent

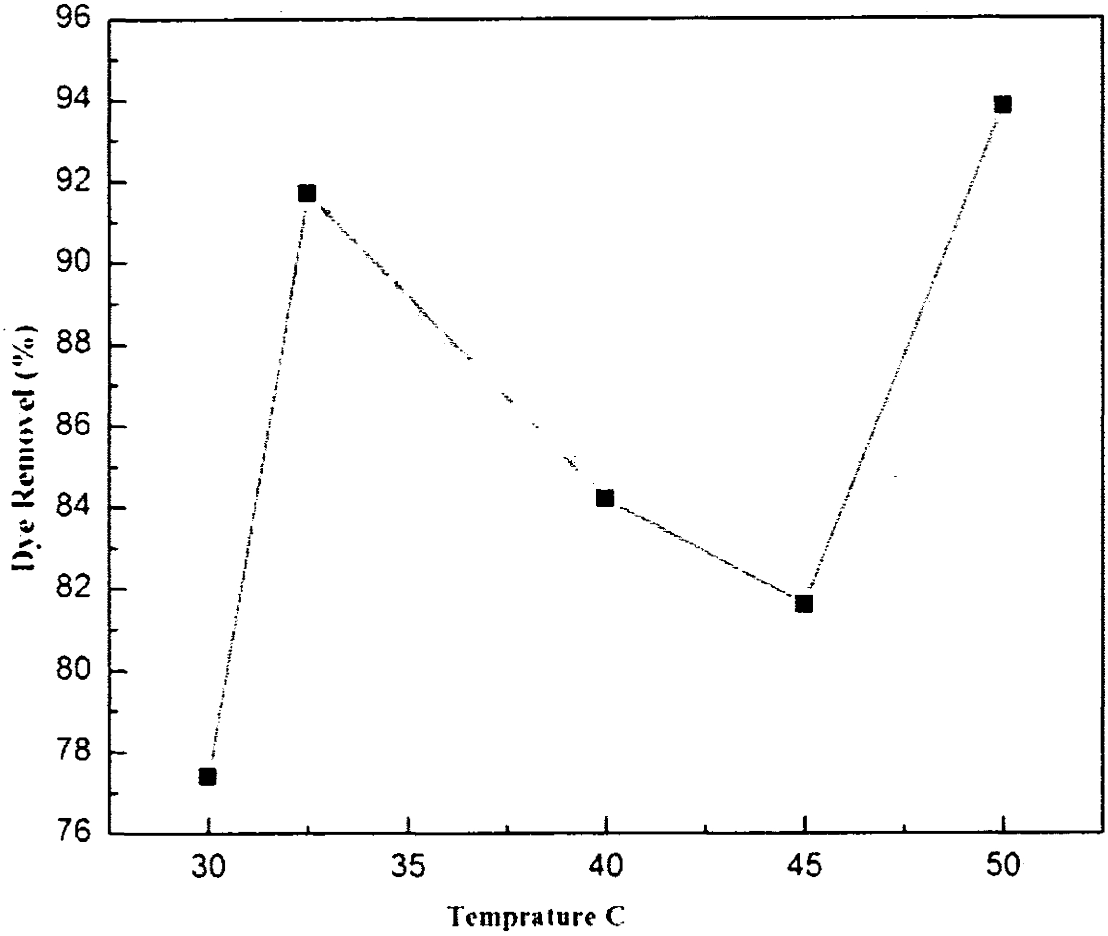

Figure 4.4 Effect of temperature on dye removal by using AC as adsorbent

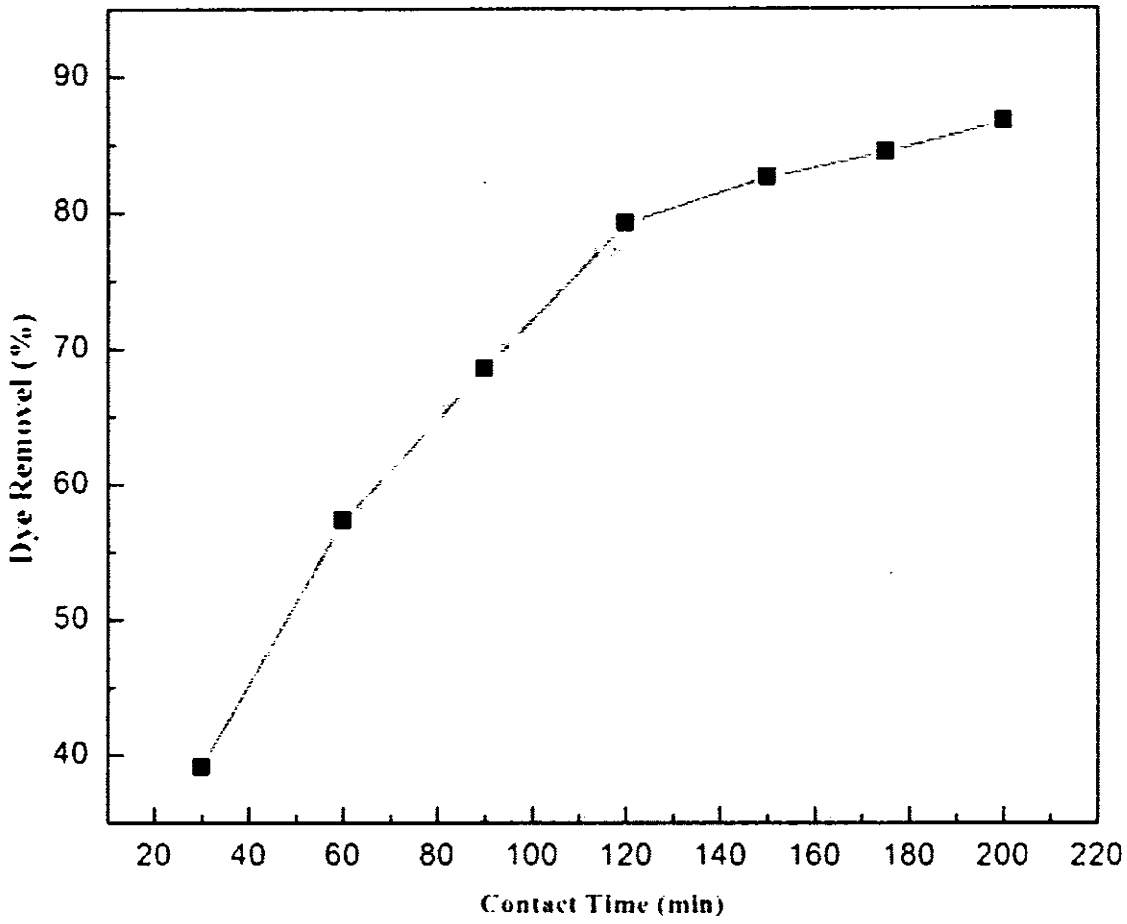

Figure 4.5 Effect of time duration on dye removal by using AC as adsorbent

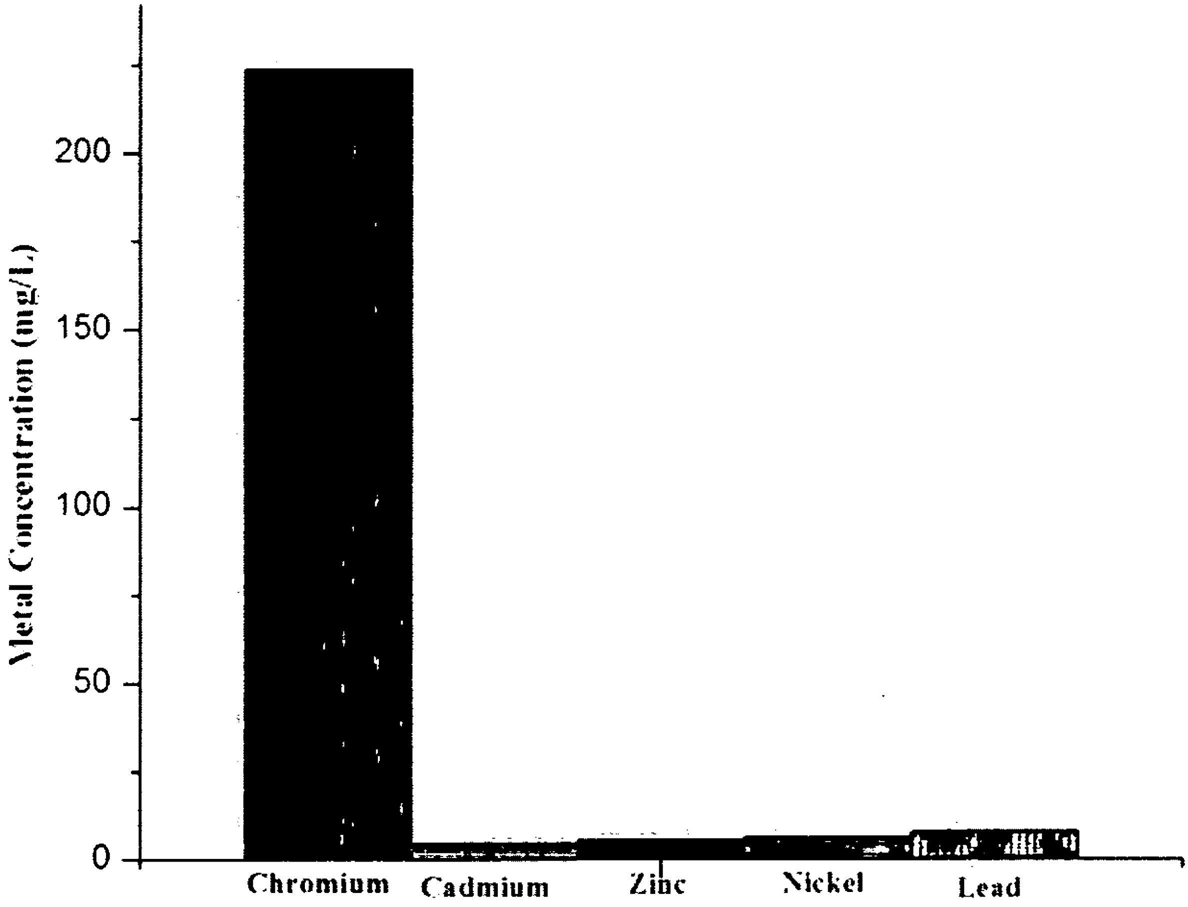

Figure 4.6 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 1

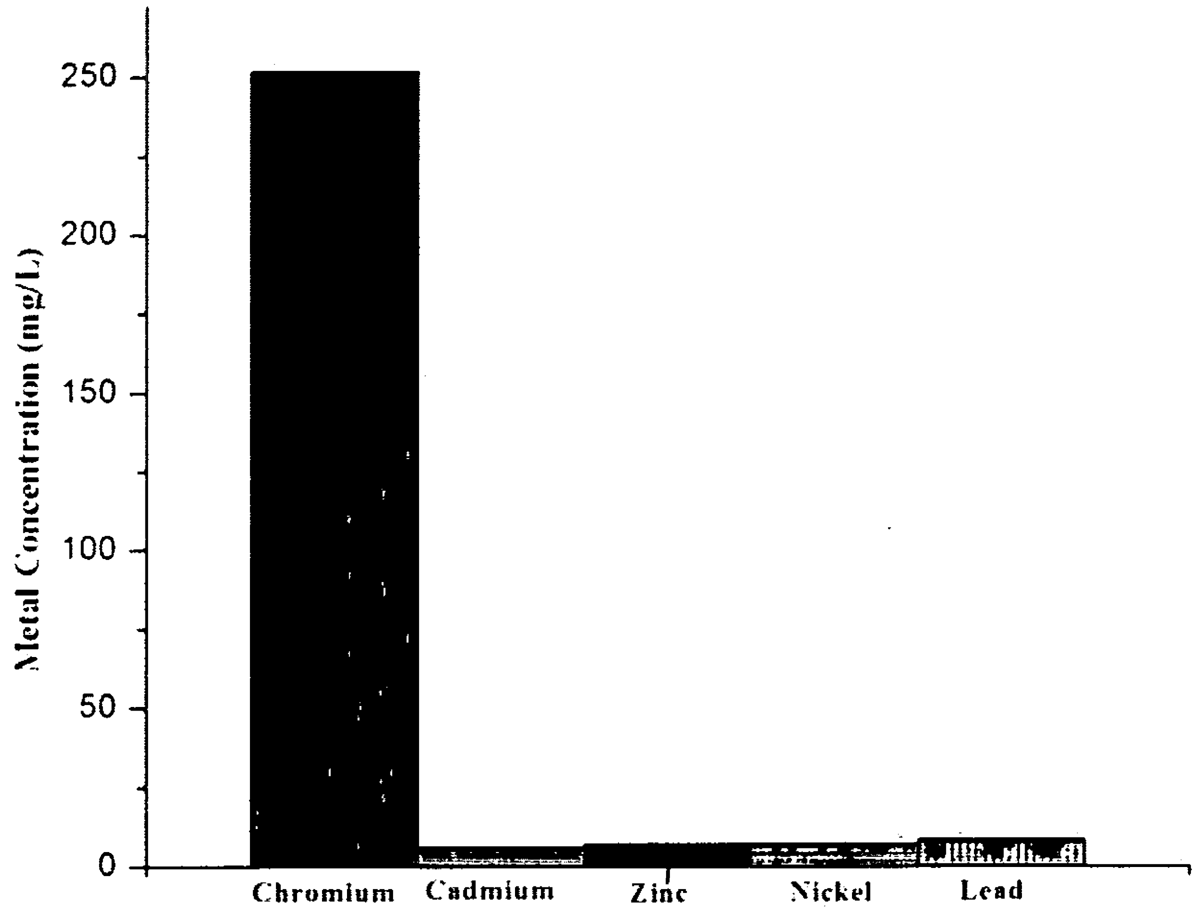

Figure 4.7 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 2

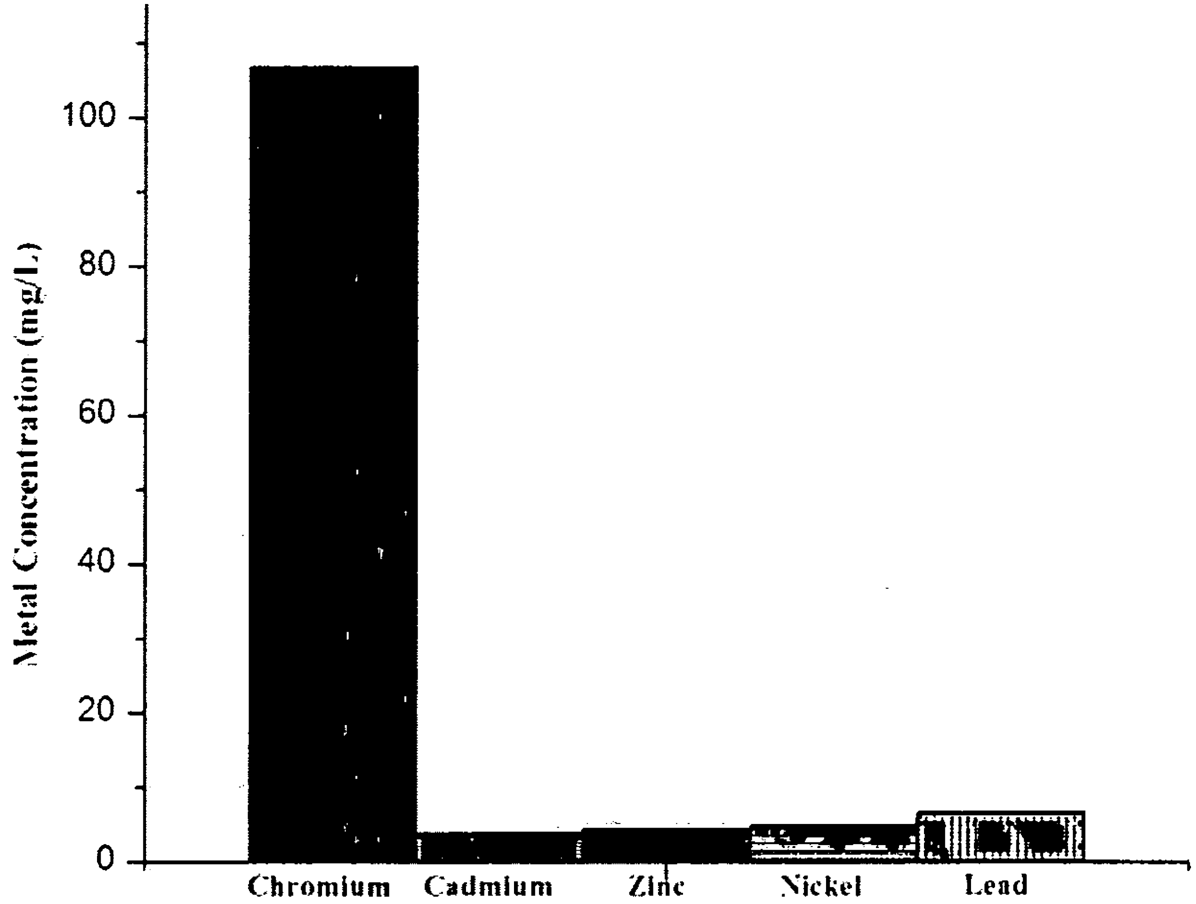

Figure 4.8 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 3

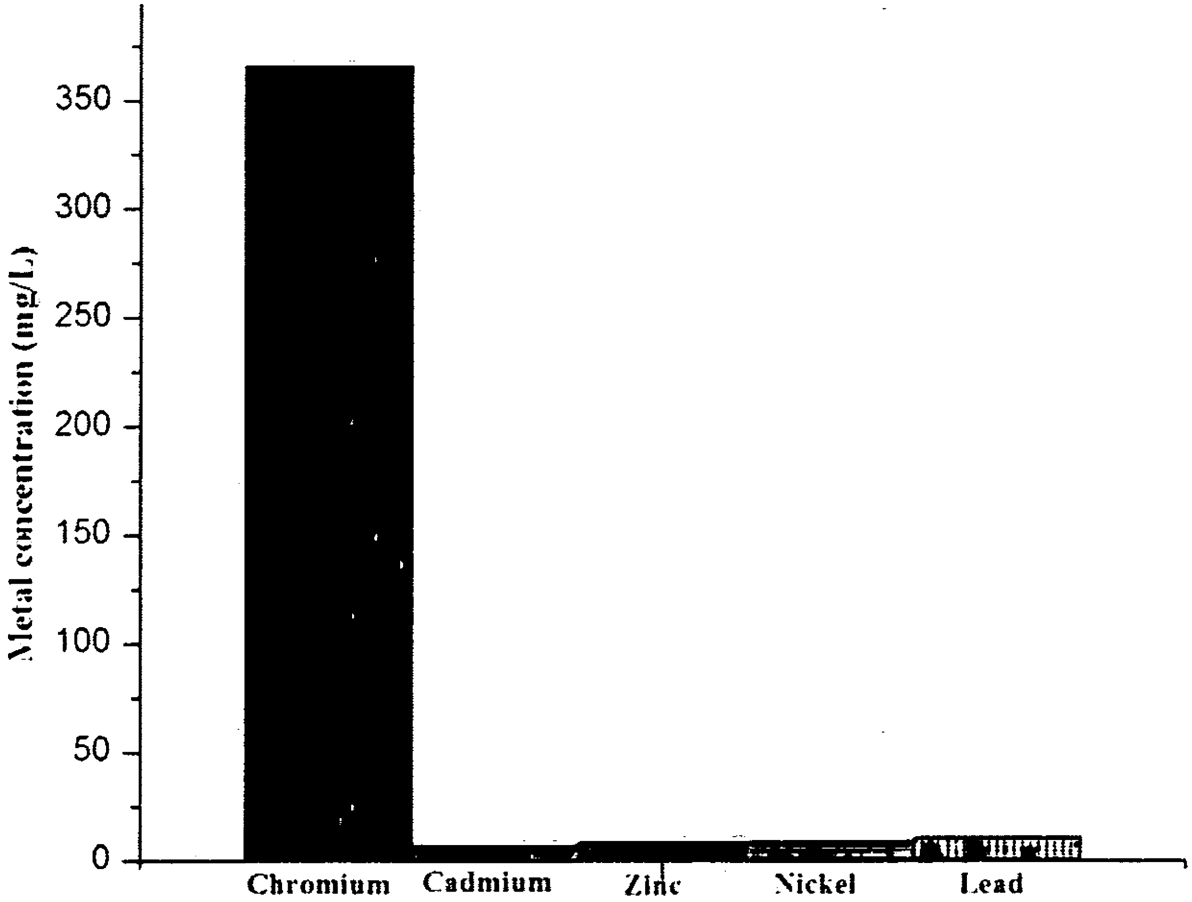

Figure 4.9 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 4

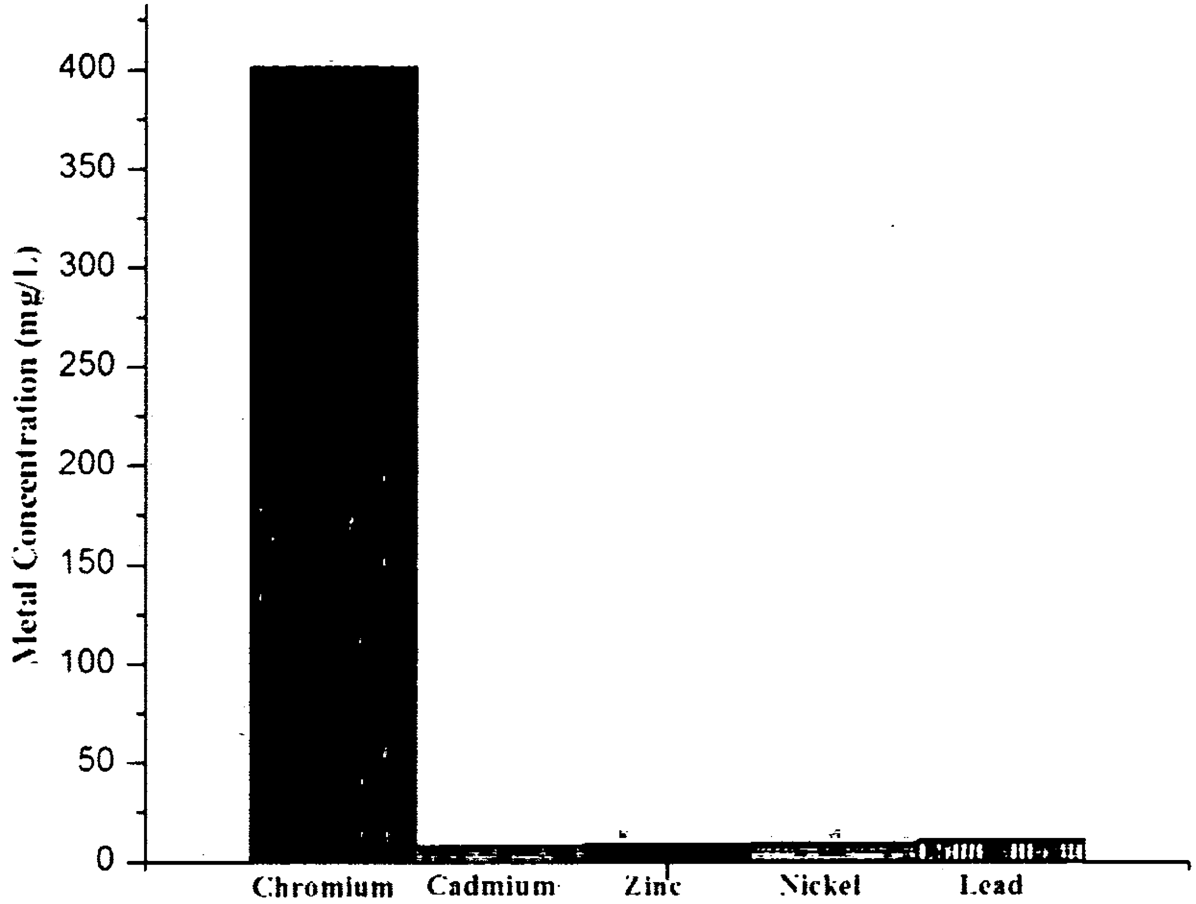

Figure 4.10 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 5

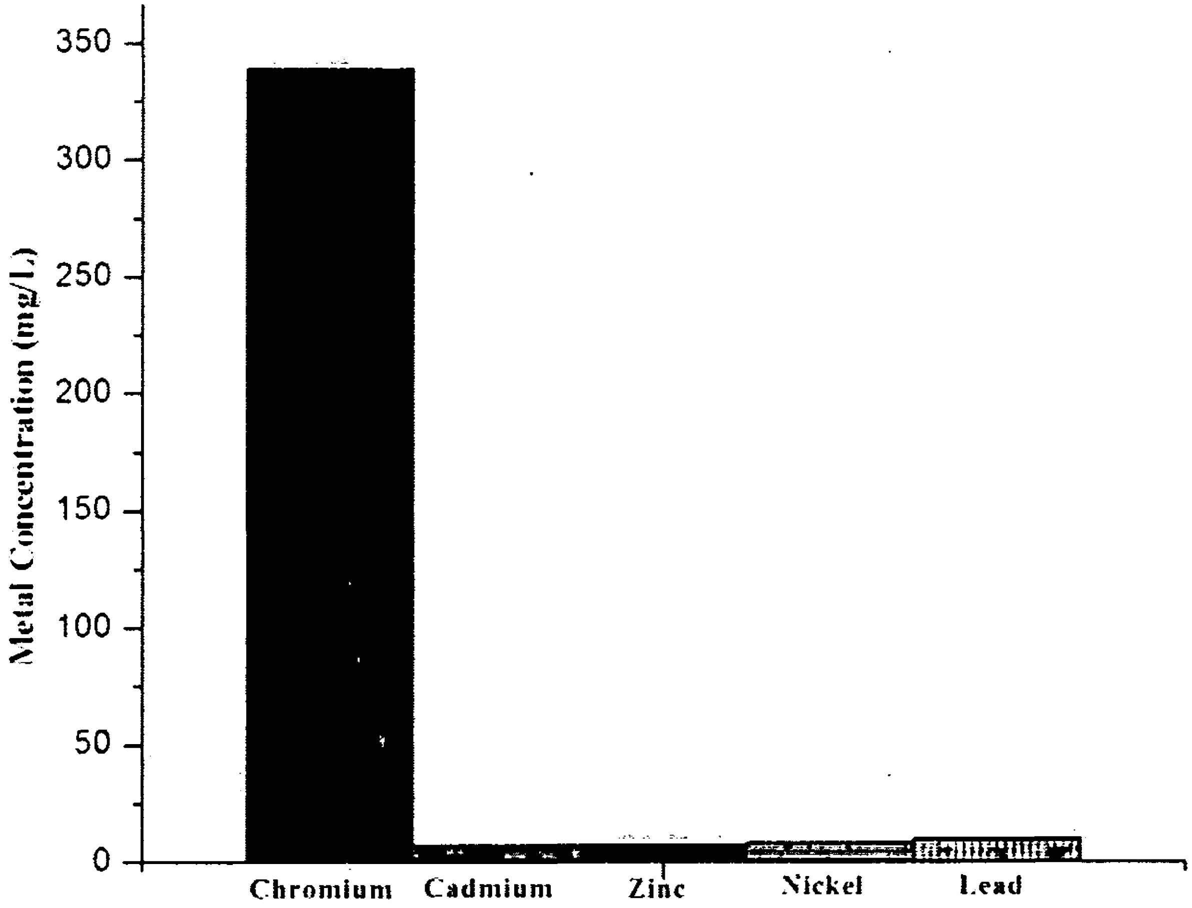

Figure 4.11 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 6

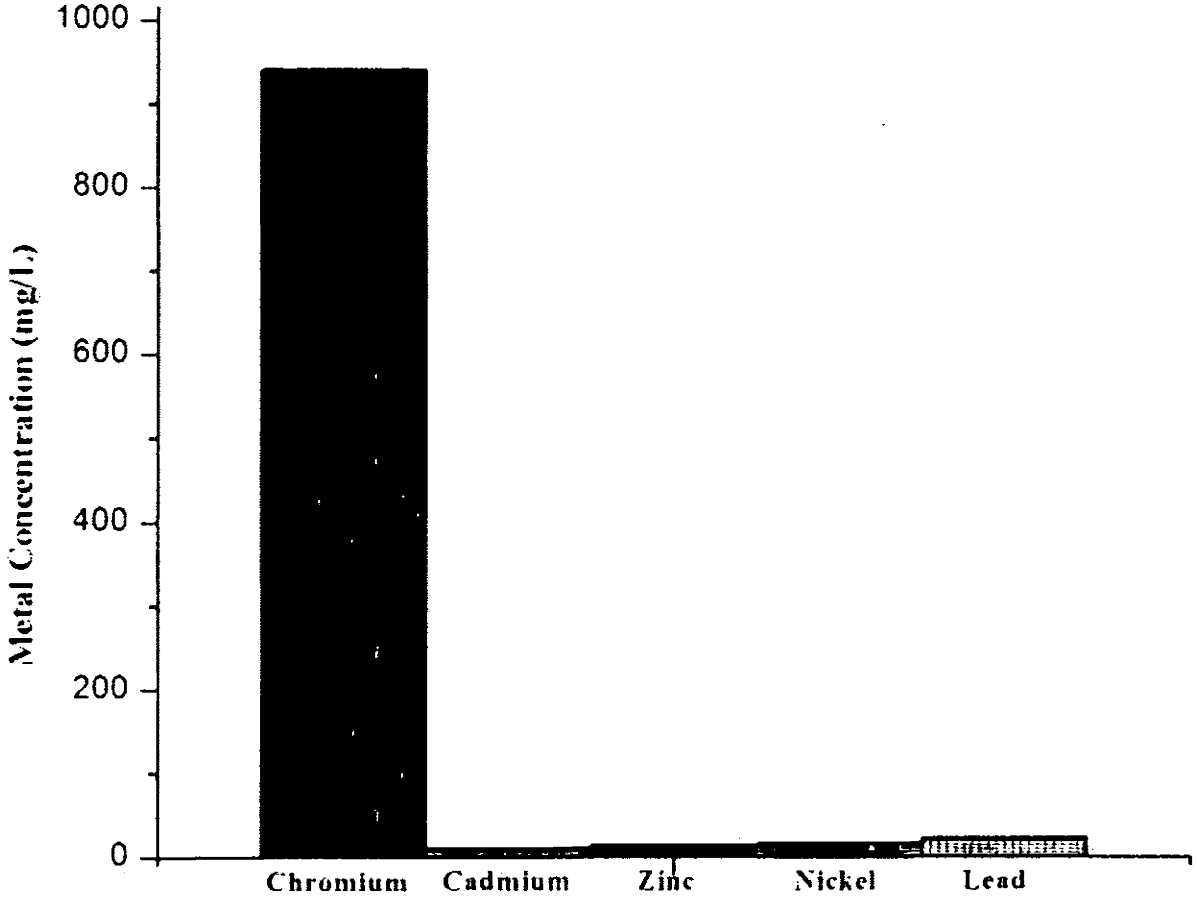

Figure 4.12 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 7

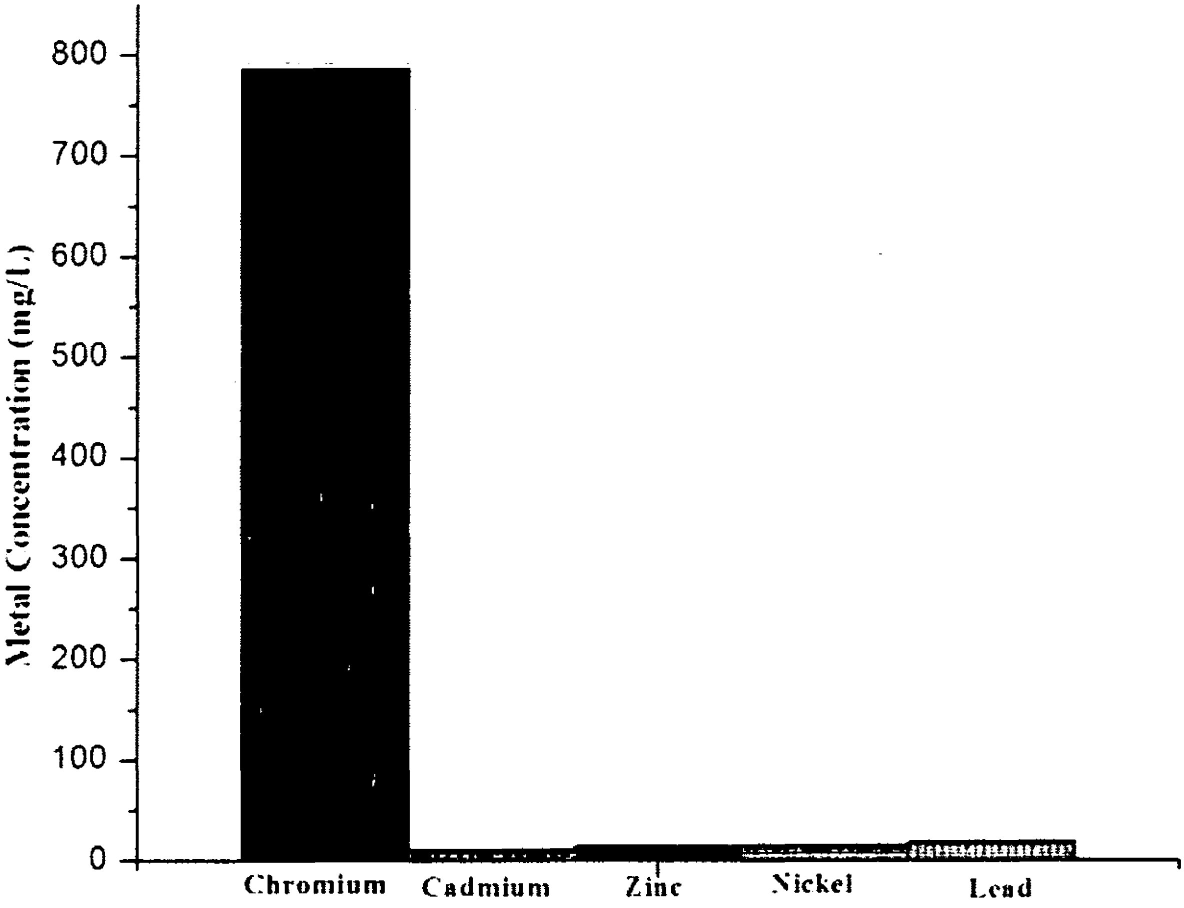

Figure 4.13 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 8

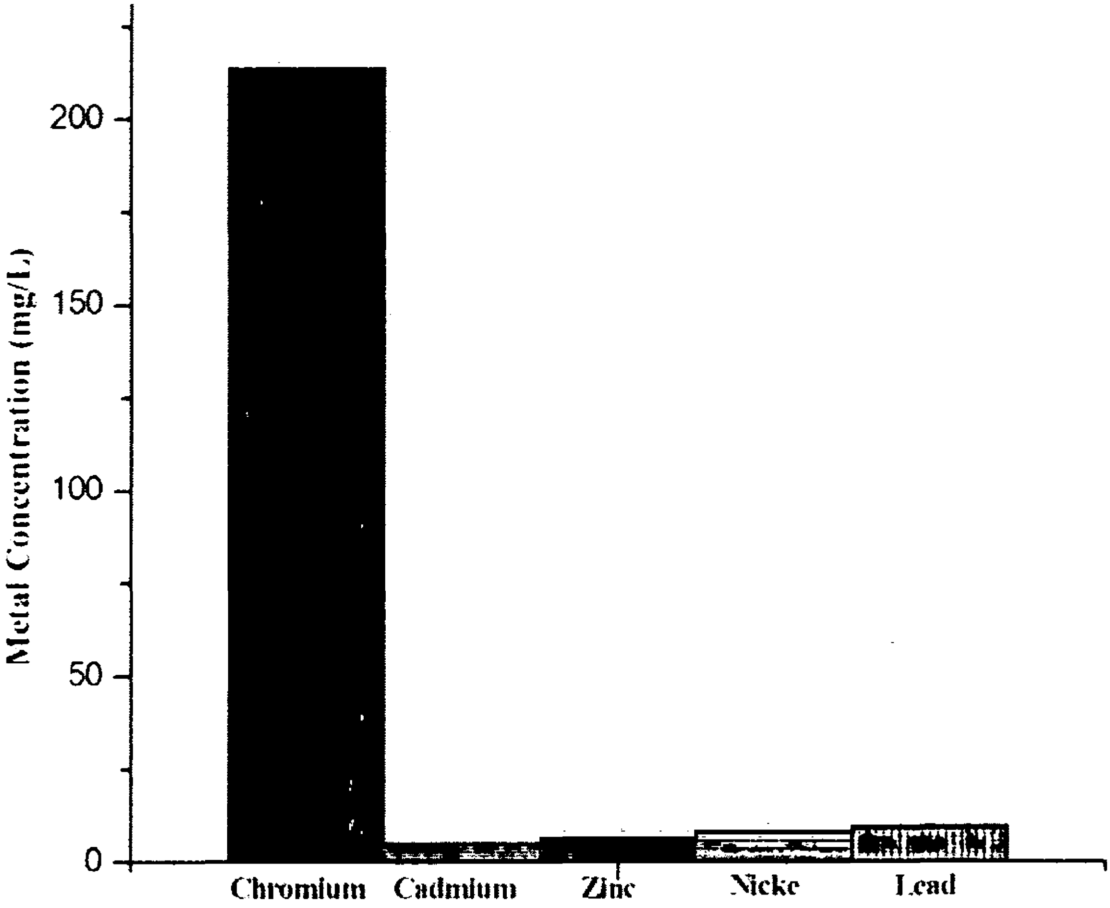

Figure 4.14 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 9

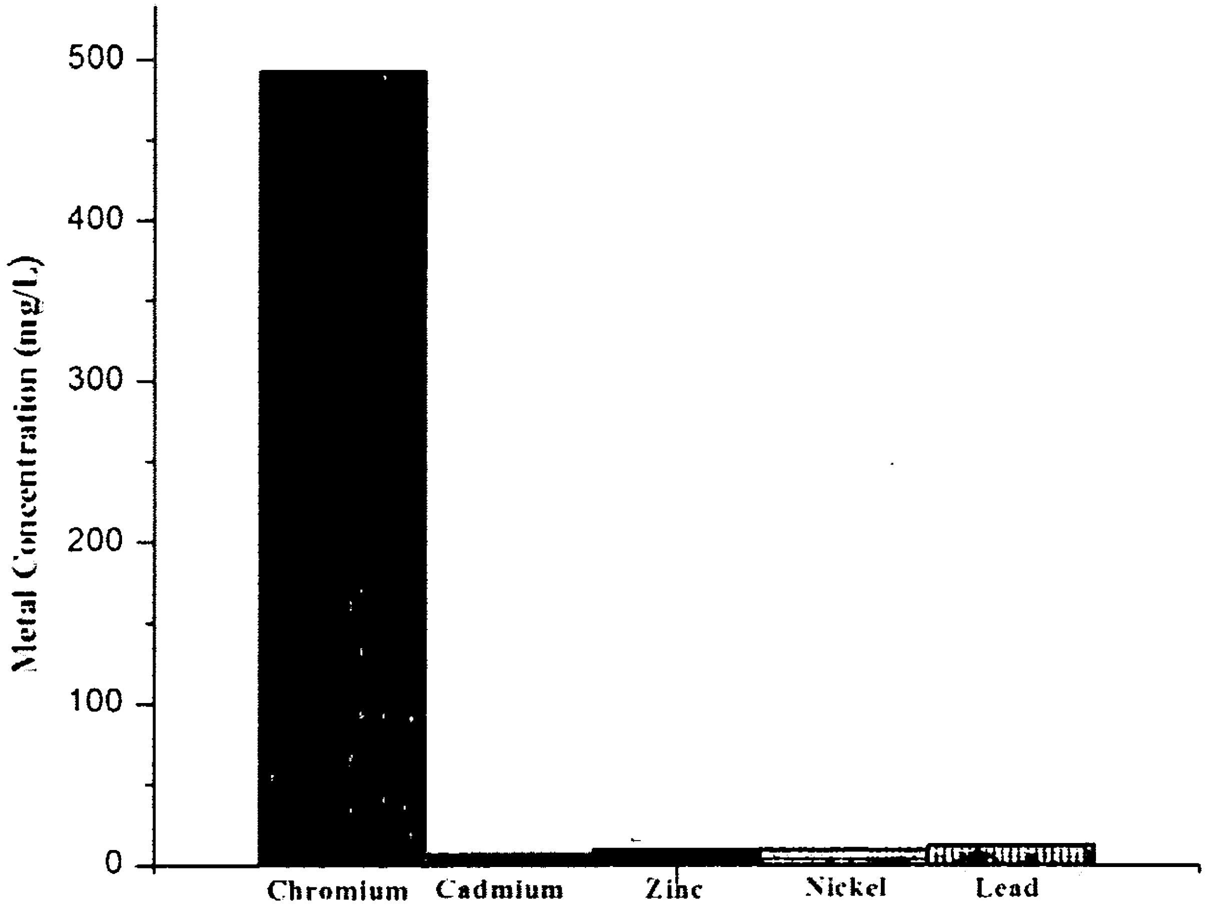

Figure 4.15 Composite Mean levels of Cr, Cd, Zn, Ni and Pb from Site 10

Chapter 5

Discussion

5. Discussion

Tannery industries discharge a huge quantity of dyes effluent which has become an important problem internationally because this effluent contains large amount of non-biodegradability compounds and huge amount of heavy metals. Dyes having wastewater cause many mortal effects and create various water born disorders e.g., cardiac arrest, hyperchloremic acidosis, hepatocellular cancer, gastroenteritis, hypertension, arteriosclerosis, sperm damage, impaired neurobehavioral functions, hepatic fibrosis, retinal toxicity, feto-maternal death and diabetes in peoples living near tanneries (Shakir *et al.*, 2012b). The diminishing physico-chemical parameters and quality of water seriously delimits its use for human consumption and for aquatic life. Therefore, the continuous and periodical monitoring of water quality is necessary so that appropriate preventive and remedial measures can be undertaken. The observations revealed that, seasonal variation has positive effect to tanneries pollution, although river water was certainly unfit for domestic and irrigation purposes without any form of treatment. Tanneries pollution generally accelerates to cause greater deterioration.

Adsorption is becoming most acceptable and preferable technique for removing dyes components from tannery effluents due to its simple process and low cost. In adsorption method, Activated carbon is used as adsorbent for dye removal and it delivers very high efficiency. Although High cost of AC is a major problem in developing countries but now waste biomass is also using to make it. Removal of dyes from tannery effluents by using AC as adsorbent is a valid and useful method. One of the key advantages associated with the use of AC is that it has very high adsorption capacity as compared to other adsorbents. Among AC, Coal made AC shows high efficiency for the removal of dye due to its pore size and surface area. But after further modification in AC, it can be more effective and its range can be extended against every kind of dyes.

Sun *et al.*, (2010) carried out an investigative study against the acid blue 193 dye by using fly ash as adsorbent. They also found that the dye removal was dependent on solution pH, dye concentration and other parameters. Chan *et al.*, (2008) investigated an adsorption study of Acid Yellow 117 and Acid Blue 25 by bamboo derived activated carbon. They found that both surface area and porosity of the carbon have played an important role in the adsorption of the dyes.

Gómez *et al.*, (2007) also performed an adsorption study of three acid dyes, Acid Red 97, Acid Orange 61 and Acid Brown 425 onto activated carbon for removal of acid dyes from aqueous solutions. They found that activated carbon was efficient at removing three acid dyes from wastewater, both in individual solutions and in mixtures. Valix *et al.*, (2004) investigated an adsorption study of Acid Blue 80 dye. Their study demonstrated that activated carbons with high acid dye adsorption capacities can be prepared from high ash bagasse based on low temperature chemical carbonisation and gasification.

The study showed that different parameters like pH, dye concentration, dose of adsorbent, agitating time and temperature have a significant role during removal of dyes through adsorption technique. It was observed that with the variation of pH was also effecting dye removal. During this parameter, removal was 76.1%, 81.7%, 84.1%, 87.2%, 71.4%, 67.6% and 63.8%. Maximum removal of 87.2% was found at pH of 6. During the dye concentration parameter, removal was 82.5%, 77.9%, 74.1% 69.8%, 61.6%, 54.2% and 42.7% respectively. Maximum removal of 82.5% was found at concentration of 50 mg/L. A rise in the early dye absorption improved the adsorption ability, but reduced the proficiency of dye removal. During parameter of dose of adsorbent, removal was 16.3%, 30.5%, 47.6%, 63.4%, 72.7%, 79.1, 81.9% and 76.6% respectively. Maximum removal of dye during this parameter was 81.9% at dose of 3 g/100mL. During using the parameter of temperature, removal was 77.4%, 91.7%, 84.2%, 81.6% and 93.8%. At temperature of 50.0 °C, maximum removal was 93.8%. When removal of dye was measured with parameter of agitating time, it was 39.1%, 57.3%, 68.5%, 79.2%, 82.6%, 84.4% and 86.7%. Maximum removal was found 86.7% at the agitating time of 200 minutes. It was showing that different parameters during adsorption have great importance. These can be effect on removal of dye. Adsorption acid blue 193 on activated carbon was also observed to be reliant on the original pH of solution.

Although tannery industry is majorly contributing in economics of Pakistan but high concentration of heavy metals is present in dye containing tannery wastewater which is becoming very harmful for the health of population living in tannery industrial area. These are causing severe health problem like osteomalacia, renal dysfunction, nephropathy, hypertension, bone degeneration, lung inefficiency, cardiac arrest and hepatocellular cancer (Yewalkar *et al.*, 2007; Guidotti *et al.*, 2008). The pH of tannery effluents ranged widely from 3.18 to 9.39 with enhanced levels of SO_4^{2-}. The concentration of various heavy metals like, Cr, Cd, Zn, Ni, and Pb were also investigated. The mean concentration of these metals was Cr, 412.57 mg/L, Cd, 6.93 mg/L, Zn, 8.53 mg/L, Ni, 9.52 mg/L and Pb, 11.59 mg/L respectively. The study demonstrated abundant higher levels of chromium in tannery effluents than measured and described before (Tunay *et. al.*, 1995; Awan *et. al.*, 2003).

It was also found that the concentration of these heavy metals was very higher then lay down by NEQS. The alterations in mean and median values indicate that distribution of metal contents in tannery effluents is not normal. This demonstrated randomized flow of effluents from the tanneries passages at times and instances not well distinct.

Conclusion and Future Work

Adsorption is very useful and significant method to remove the dyes and other contaminants from tannery as well as other industrial wastewater. For this purpose, Activated Carbon prepared from coal and other biomass is most attractive adsorbent because it has more ability to adsorb the contaminants from wastewater as compared to other adsorbents. Therefore, there is a rising trend in using low cost, simply available AC prepared from biomass material for the adsorption of dye colors.

There is a need of prevention measure for management of tannery effluents industry in Kasur and other cities having tannery industry. Because within time, health damage from tannery effluent is rapidly increasing. It is need to implement more efficient leather cleaning technologies. Besides, there is a much necessity to recognize the hazards associated to the tanning industry and for realizing and imposing ecological strategies through technology allocation. Tanning processes produce pollution but if they are prohibited, reprocessed and then preserved, the manufacture can be further safe and maintainable otherwise few years from now, serious water quality deterioration could take place, which will serious threat to aquatic and human life.

A clear industrial policy is required which integrates ecofriendly purposes at par with the more conformist financial ideas of better service, value added, import exchange and export elevation to alternate the dilemma of the leather trade sector increasingly near a less contaminating position and expand the productivity and worth of methods used.

The effective and actual controlling of the chrome wastes and chrome tanning procedure in a tannery are main anxieties in an efficacious task. Chrome managing objectives at refining chrome consumption in tanning processes to an extreme degree in directive to exploit the quantity of chrome liquidated into emissions. In conclusion it may be emphasized that accomplishment of maintainable trade expansion would confirm substantial developments at all stages of the tanning progression.

References

References

Agget P.J., And Comerford J.G., (1995) Zinc and human health, Nutrition Reviews, 53, p. 2-16

Ahmad M.Z., And Rahman N.K., (2011) Equilibrium, kinetics and thermodynamics of Remazol Briliian Orange 3R dye adsorption on coffee husk-based activated carbon, Chemical Engineering Journal, 170, p. 154–161

Ahmed M.J., And Dhedan S.K., (2012) Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons, Fluid Phase Equilibra, 317, p. 9–14

Alaya M., Hourieh M., Youssef A., And El-Sejarah F., (1999) Adsorption properties of activated carbons prepared from olive stones by chemical and physical activation, Adsorption Science & Technology, 18, p. 27–42

Ali I., Asim M., And Khan T.A., (2012) Low cost adsorbents for the removal of organic pollutants from wastewater, Journal of Environmental Management 113, p. 170-183

Altenor S., Carene B., Emmanuel E., Lambert J., Ehrhardt J.J., And Gaspard S., (2009) Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, Journal of Hazardous Materials, 165, p. 1029–1039

Asgher M., And Bhatti H.N., (2012) Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions, Ecological Engineering, 38, p. 79– 85

Attia A.A., Girgis B.S., And Fathy N.A., (2008) Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: batch and column studies, Dyes Pigments, 76, p. 282–289

Augustus T., (1996) The Pakistan Leather Industry (LEATHER), http://www.american.edu/project/mandala/TED/leatherhtm

Awan M.A., Baig M.A., Iqbal J., Aslam M.R., And Ijaz N., (2003) Recovery of chromate from tannery wastewater, Electronic Journal of Environmental Agricultural and Food Chemistry, 2, p. 543-548

Axtell N.R., Sternberg S.P.K., And Claussen K., (2003) Lead and nickel removal using Microspora and *Lemna minor*, Bioresource Technology, 89, p. 41-48

Aygun A., Yenisoy-Karakas S., And Duman I., (2003) Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties, Microporous Mesoporous Mater, 66, p. 189–195

Balakrishnana P.A., Arunagiria A., And Rao P.G., (2002) Ozone generation by silent electric discharge and its application in tertiary treatment of tannery effluent, Journal of Electrostatics, 56, p. 77–86

Banat F., Al-Asheh S., Al-Ahmad R., And Bni-Khalid F., (2007) Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal, Bioresource Technology, 98, p. 3017–3025

Banat F., Al-Asheh S., And Al-Makhadmeh L., (2003) Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochemistry, 39, p. 193–202

Banat I.M., Nigam P., Singh D., And Marchant R., (1996) Microbial decolorization of textile dye containing effluents: A Review, Bioresource Technology, 58, p. 217-227

Baral A., And Engelken R.D., (2002) Chromium-based regulations and greening in metal finishing industries in the USA, Environmental Science & Policy, 5, p. 121–133

Baruthio F., (1992) Toxic effects of chromium and its compounds, Biological Trace Element Research, 32, p. 145-153

Basar C.A., (2006) Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, Journal of Hazardous Materials, 135, p. 232–241

Bestani B., Benderdouche N., Benstaali B., Belhakem M., And Addou A., (2008) Methylene blue and iodine adsorption onto an activated desert plant, Bioresourse Technology, 99, p. 8441–8444

Bosnic M., Buljan J., And Daniels R.P., (2000) Pollution in tannery effluents, US/RAS/92/120, UNIDO Regional program for pollution control in tanning industry in South East, Asia

Bulut E., Ozacar M., And Sengil I.A., (2008) Equilibrium and kinetic data and process design for adsorption of Congo red on bentonite, Journal of Hazardous Materials, 154, p. 613-622

Bussi J., Ohanian M., Vazquez M., And Dalchiele E.A., (2002) Photocatalytic removal of Hg from solid wastes of chlor-alkali plant, Journal of Environmental Engineering, 128, p. 733-742 carbon: A critical review, Journal of American Water Works Association, 83, p. 65–76

Chan L.S., Cheung W.H., McKay G., (2008) Adsorption of acid dyes by bamboo derived activated carbon, Desalination, 218, p. 304–312

Chandra T.C., Mirna M.M., Sudaryanto Y., And Ismadji S., (2007) Adsorption of basic dye on to activated carbon prepared from durian shell: studies of adsorption equilibrium and kinetics, Chemical Engineering Journal, 127, p. 121–129

Cheng M.M., Ma W.H., Li J., Huang Y.P., And Zhao J.C., (2004) Visible-light-assisted degradation of dye pollutants over Fe(III)-loaded resin in the presence of H_2O_2 at neutral pH values, Environmental Science & Technology, 38, p. 1569–1575

Chiou M.S., And Li H.Y., (2002) Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, Journal of Hazardous Materials, 93, p. 233–248

Costa C.R., Botta C.M.R., Espindola E.L.G., And Olivi P., (2008) Electrochemical treatment of tannery wastewater using DSA (R) electrodes, Journal of Hazardous Materials, 153, p. 616–627

Crini G., (2006) Non-conventional low-cost adsorbents for dye removal: A review. Bioresource Technology, 97, p. 1061–1085

Dabrowski A., (2001) Adsorption, from theory to practice, Advances in Colloid and Interface Science, 93, p. 135-224

Dasgupta S., (1998) Minimising the environmental impact of chrome tanning: the thrublu process, Journal of the Society of Leather Technologists and Chemists, 82, p. 15-21

Deng H., Lu J., Li G., Zhang G., And Wang X., (2011) Adsorption of methylene blue on adsorbent materials produced from cotton stalk, Chemical Engineering Journal, 172, p. 326–334

Dogruel S., Genceli E.A., Babuna F.G., And Orhan D., (2006) An investigation on the optimal location of ozonation within biological treatment for a tannery wastewater, Journal of Chemical Technology and Biotechnology, 81, p. 1877–1885

Durai G., And Rajasimman M., (2011) Biological treatment of tannery wastewater- A review, Juornal of environmental science and technology, 4, p. 1-17

Dutta S., Bhattacharyya A., Ganguly A., Gupta S., And Basu S., (2011) Application of response surface methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of methylene blue, Desalination, 275, p. 26– 36

EEC black list substances., (1976) EEC Directive 76/464/EEC (OJL129 18.5.76)

El Qada E.N., Allen S.J., And Walker G.M., (2008) Adsorption of basic dyes from aqueous solution onto activated carbons, Chemical Engineering Journal, 135, p. 174–184.

Foo K.Y., And Hameed B.H., (2012) Microwave-assisted regeneration of activated carbon. Bioresource Technology, 119, p. 234–240

Forgacs E., Cserhati T., And Oras G., (2004) Removal of synthetic dyes from wastewater: A review, Environment International, 30, 953-971

Galiana-Aleixandre M.V., Mendoza-Roca J.A., And Bes-Pia A., (2011) Reducing sulfates concentration in the tannery effluent by applying pollution prevention techniques and nanofiltration. Journal of Cleaner Production, 19, p. 91–98

Garg V.K., Amita M., Kumar, R., And Gupta R., (2004) Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste, Dyes Pigments, 63, p. 243-250

Gómez, V., Larrechi M.S., And Callao M.P., (2007) Kinetic and adsorption study of acid dye removal using activated carbon, Chemosphere, 69, p. 1151–1158

Government of India, Ministry of Health and Family Welfare., (2000) Notification GSR759 (E)

Goyer R.A., (1996) Toxic effect on metals In: Casarett & Doull's Toxicology, The Basic Science of Poisons, 5th ed, Klaassan C.D (ed), McGraw Hill Health Profession Division, ISBN 0071054766

Guidotti T.L., Namara M.J., Mosses M.S., (2008) The interpretation of trace element analysis in body fluids, Indian Journal of Medical Research, 128, p. 524-532.

Guo J., Luo Y., Lua A.C., Chi R.A., Bao X.T., And Xiang S.X., (2007) Adsorption of hydrogen

Gupta V.K., And Suhas., (2009) Application of low-cost adsorbents for dye removal: A review, Journal of Environmental Management, 90, p. 2313–2342

Gurses A., Dogar C., Karaca S., Acikyildiz M., And Bayrak R., (2006) Production of granular activated carbon from waste Rosa canina sp. seeds and its adsorption characteristics for dye, Journal of Hazardous Materials, 131, p. 254–259

Hage R., And Lienke A., (2006) Applications of transition-metal catalysts to textile and wood-pulp bleaching, Angewandte Chemie International Edition, 45, p. 206–222

Hameed B.H., Din A.T.M., And Ahmad A.L., (2007a) Adsorption of methylene blue on to bamboo-based activated carbon: kinetics and equilibrium studies, Journal of Hazardous Materials, 141, p. 819–825

Hameed B.H., Ahmad A.L., And Latiff K.N.A., (2007b) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes Pigments, 75, p. 143–149

Hameed B.H., Tan I.A.W., And Ahmad A.L., (2008a) Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology, Journal of Hazardous Materials, 158, p. 324–332

Hameed B.H., And Daud F.B.M., (2008b) Adsorption studies of basic dye on activated carbon derived from agricultural waste: Hevea brasiliensis seed coat, Chemical Engineering Journal 139, p. 48–55

Haro M., Ruiz B., Andrade M., Mestre A.S., Parra J.B., Carvalho A.P., And Ania C.O., (2012) Dual role of copper on the reactivity of activated carbons from coal and lignocellulosic precursors, Microporous and Mesoporous Materials, 154, p. 68–73

Hekstra G.P., (1995) Delayed effects of pollutants in soil and sediments: understanding and handling of chemical time bombs in Europe, Economics script, p. 56

Houshyar Z., Khoshfetrat A.B., And Fatehifar F., (2012) Influence of ozonation process on characteristics of pre-alkalized tannery effluents, Chemical Engineering Journal, 191, p. 59– 65

Iqbal M., (1998) The leather sector report, http://www.copper.org.pk/etpirpt/leather sectorreportpdf

Jarup L., (2002) Cadmium overload and toxicity, Nephrol Dial Transplant, 17: p, 35-39

Jiang Z., Wang H., Huang H., And Cao C., (2004) Photocatalysis enhancement by electric field: TiO_2 thin film for degradation of dye X-3B, Chemosphere, 56, p. 503–508

Jiuhui Q.U., (2008) Research progress of novel adsorption processes in water purification: A review, Journal of Environmental Sciences, 20, p. 1-13

Kabata-Pendias A., And Pendias H., (1979) Trace elements in biological habitat, Wydawnictwo Geologiczene, Warsaw, p. 171-176

Kabra K., Chaudhary R., And Sawhney R.L., (2004) Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: A review, Industrial Engineering Chemistry Research, 43, p. 7683-7696

Kannan N., And Sundaram M.M., (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons: A comparative study, Dyes Pigments, 51, p. 25–40

Kavitha D., And Namasivayam C., (2007) Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresourse Technology, 98, p. 14–21

Kim T.H., Park C., Yang J.M., And Kim S., (2004) Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation, Journal of Hazardous Materials, 112, p. 95–103

Legrouri K., Khouyab E., Ezzinea M., Hannachea H., Denoyelc R., Pallierd R., And Naslaind R., (2005) Production of activated carbon from a new precursor molasses by activation with sulphuric acid, Journal of Hazardous Materials, 118, p. 259–263

Letterman R.D., (1999) Water quality and treatment: a handbook of community water supplies, American Water Works Association, McGraw Hill Publication, New York

Lian L., Guo L., And Guo C., (2009) Adsorption of congo red from aqueous solution on Ca-bentonite, Journal of Hazardous Materials, 161, p. 126-131

Lin Y., And Teng H., (2002) Mesoporous carbons from waste tire char and their application in wastewater discoloration, Microporous Mesoporous Mater, 54, p. 167–174

Linsebigler A.L., Lu G., And Yates J.T., (1995) Photocatalysis on TiO_2 surfaces: principles, mechanisms and selected results, Chemical Reviews, 95, p. 735-748

Liu C.-H., Wu J.-S., Chiu H.-C., Suen S.-Y., And Chu K.H., (2007) Removal of anionic reactive dyes from water using anion exchange membranes as adsorbers, Water Research, 41, p. 1491−1500

Ma D.Y., Wang X.W., Song C., Wang S.G., Fan M.H., And Li, X.M., (2011) Aerobic granulation for methylene blue biodegradation in a sequencing batch reactor, Desalination, 276, p. 233–238

MacKay D., And Diamond M., (2003) Application of the QWASI (Quantitative Water Air Sediment Interaction) fugacity model to the dynamics of organic and inorganic chemicals in lacks, Chemosphere, 18, p. 1343-1365

Madaeni S.S., Jamali Z., And Islami N., (2011) Highly efficient and selective transport of methylene blue through a bulk liquid membrane containing Cyanex 301 as carrier, Separation and Purification Technology, 81, p. 116–123

Martinez-Hutile A.C., And Brillas E., (2009) Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review, Applied Catalysis B: Environmental, 87, p. 105-145

McKay G., (1996) Use of adsorbents for the removal of pollutants from wastewaters, CPS Press, New York

Meric S., Kaptan D., And Tunay C., (2003) Removal of color and COD from a mixture off our reactive azo dyes using Fenton oxidation process, Journal of Environmental Science and Health, Part A, Toxic/hazardous Substances & Environmental Engineering, 38, p. 2241–2250

Mishra G., And Tripathy M., (1993) A critical review of the treatment for decolorization of textile effluent, Colour age 40, p. 35-38

Mona S., Kaushik A., And Kaushik C.P., (2011) Biosorption of reactive dye by waste biomass of Nostoc linckia, Ecological Engineering, 37, p. 1589–1594

More S.V., John S., Rao B.S., Nair B.U., And Laxman R.S., (2001) Chromium removal and reduction of COD of tannery effluents by actinomycetes, Indian Journal of Environmental Health, 43, p. 108-113

Morita M., Ito R., Kamidate T., And Watanabe H., (1996) Kinetics of peroxidase catalyzed decoloration of Orange II with hydrogen peroxide, Textile Research Journal, 66, p. 470–473

Mu Q., Li, Y., Zhang Q., And Wang H., (2011) TiO_2 nanofibers fixed in a microfluidic device for rapid determination of chemical oxygen demand via photoelectrocatalysis, Sensors and Actuators B, Chemical,155, p. 804–809

References

Mudoga H.L., Yucel H., And Kincal N., (2008) Decolorization of sugar syrups using commercial and sugar beet pulp based activated carbons, Bioresource Technology, 99, p.3528–3533

Najm I.N., Snoeyink V.L., Lykins B.W.J., And Adams J.Q., (1991) Using powdered activated carbon: a critical review, Journal of American Water Works Association, 83, p. 65–76

Namboodri C.G., Perkins W.S., And Walsh W.K., (1994a) Decolorizing dyes with chlorine and ozone: Part I, American Dyestuff Reporter, 83, p. 17–22

Namboodri C.G., Perkins W.S., Walsh W.K., (1994b) Decolorizing dyes with chlorine and ozone: Part II, American Dyestuff Reporter 83, p. 17–26

Nandi B.K., Goswami A., And Purkait M.K., (2009) Removal of cationic dyes from aqueous solutions by kaolin: Kinetic and equilibrium studies, Applied Clay Science, 42, p. 583-590

National Environmental Quality Standards (NEQS)., (1999) Pakistan Environmental Protection Agency, Government of Pakistan

Omura T., (1994) Design of chlorine-fast reactive dyes for degradation of amino containing azo dyes by sodium-hypochlorite, Dyes Pigments, 26, p. 33–50

Ozer A., And Dursun G., (2007) Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon, Journal of Hazardous Materials, 146, p. 262–269

Packham R.F., (1996) Drinking water quality and health, In: Harrison R M (ed) Pollution: Causes effect and control 3rd ed, The Royal Society of Chemistry, UK, p. 52-65

Parikh J.K., Sharma V.K., Gosh U., And Panda M.K., (1995) Trade and Environmental Linkages: A case study of India, Indira Gandhi Institute of Development Research, Report Prepared by UNCTAD

Pasco N., Baronian K., Jeffries C., Webber J., And Hay J., (2004) MICREDOX®—development of a ferricyanide-mediated rapid biochemical oxygen demand method using an immobilized *Proteus vulgaris* biocomponent, Biosensors and Bioelectronics, 20, p. 524–532

Piccin J.S., Gomes C.S., Feris L.A., And Gutterres M., (2012) Kinetics and isotherms of leather dye adsorption by tannery solid waste, Chemical Engineering Journal, 183, p. 30– 38

PNEP: Pakistan National Environmental Plan (1991) National Conservation Strategy, p. 322

Pojer P.M., And Huynch C.P., (1999) process of the XXVIULTCS Congress Madras (India), p. 308-313

Preethi V., Parama Kalyani K.S., Iyappan K., Srinivasakannan C., Balasubramaniam N., And Vedaraman N., (2009) Ozonation of tannery effluent for removal of cod and color, Journal of Hazardous Materials, 166, p. 150–154

Raghu S., And Basha A.C., (2007) Chemical or electrochemical techniques, followed by ion exchange, for recycle of textile dye wastewater, Journal of Hazardous Materials, 149, p. 324−330

Ramasami T., Sreeram K.J., And Gayatri R., (1997) Design operation and maintenance of effleunt treatment plants, Paper presented in regional workshop, p, 20

Rathindra N.B., Fonkeng B., David G.B., Farrell R.P., Judd R.P., Lay P.A., And Sangster D.F., (1996) Redox potential of Chromium (V)/(IV), (V)/(III) and (IV)/(III) complexes with 2-ethyl-2-hydroxybutanoato (2-/1-) ligands, journal of American Chemical Society, 118, p. 7139-7144

Reddy V.R., And Behera H., (2006) Impact of water pollution on rural communities: an economic analysis, Ecological Economics, 58, p. 520–537

Rehman M.A., (1996) Health impact assessment of tanning industrial activity in Kasur Pakistan in: research report, Human Settelment Development Program, School of Environmental Resources and Development (SERD), Asian Institute of Technology, Thailand, p. 1-18

Robinson T., McMullan G., Marchant R., And Nigam P., (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, Bioresource Technology, 77, p. 247-255

Salbu B., KreKling T., And Oughton D.H., (1988) Characterization of radioactive particles in the environment, Analyts, 123, p. 843-849

Saniz-Diaz C., And Griffiths A., (2000) Activated carbon from solid wastes using a pilot scale batch flaming pyrolyser, Fuel, 79, p. 1863–1871

Senthilkumaar S., Varadarajan P.R., Porkodi K., And Subbhuraam C.V., (2005) Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, Journal of Colloid and Interface Science, 284, p. 78–82

Shabbir K., (1995 a) Leather Garments, Pakistan & Gulf Economist, p, 10

Shabbir K., (1995 b) Exports: Lets broaden our vision, Pakistan and Gulf Economist, p 10-11

Shakir L., Ejaz S., Ashraf M., Qureshi N.A., Anjum A.A., Iltaf I., And Javeed A., (2012a) Ecotoxicological risks associated with tannery effluent wastewater, environmental toxicology and pharmacology, 34, p. 180–191

Shakir L., Ejaz S., Ashraf M., Ahmad N., And Javeed A., (2012b) Characterization of tannery effluent wastewater by proton-induced X-ray emission (PIXE) analysis to investigate their role in water pollution, Environmental Science and Pollution Research International, 19, p. 492–501

Srinivasan SV., Rema T., Chitra K., Balakameswari K.S., Suthantharanjan R., Maheswari B.U., Ravindranath E., And Rajamani S., (2009) Decolourisation of leather dye by ozonation, Desalination, 235, p. 88-92

Srivastava S., Mishra S., Dwivedi S., Baghel V.S., Verma S., Tandon P.K., Rai U.N., And Tripathi R.D., (2005) Nickel Phytoremediation Potential of Broad Bean, *Vicia faba* L., and Its Biochemical Responses. Bulletin of Environmental Contamination and Toxicology, 74, p. 715-724

Stavropoulos G.G., And Zabaniotou A.A., (2005) Production and characterization of activated carbons from olive-seed waste residue, Microporous Mesoporous Mater, 82, 79–85

sulphide (H_2S) by activated carbons derived from oil-palm shell, Carbon, 45, p. 330–336

Sun D., Zhanga X., Wub Y., And Liu X., (2010) Adsorption of anionic dyes from aqueous solution on fly ash, Journal of Hazardous Materials, 181, p. 335–342

Sundrarajan M., Vishnu G., And Joseph K., (2007) Ozonation of light-shaded exhausted reactive dye bath for reuse, Dyes Pigments, 75, p. 273–278

Szpyrkowicz L., Kelsall G.H., Kaul S.N., And De Favei M., (2001) Performance of electrochemical reactor for treatment of tannery wastewaters, Chemical Engineering Science, 56, p. 1579–1586

Tahir S.S., And Naseem R., (2007) Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay, Separation and Purification Technology, 153, p. 312–321

Tamai H., Kakii T., Hirota Y., Kumamoto T., And Yasuda H., (1996) Synthesis of extremely large mesoporous activated carbon and its unique adsorption for giant molecules, Chemistry of Materials, 8, p. 454–462

Tan I.A.W., Ahmad A.L., And Hameed B.H., (2008) Adsorption of basic dye on high surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, Journal of Hazardous Materials, 154, p. 337–346

Tan I.A.W., Ahmad A.L., And Hameed B.H., (2008) Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination, 225, p. 13–28

Tan I.A.W., Hameed B.H., And Ahmad A.L., (2007) Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, Chemical Engineering Journal, 127, p. 111–119

Tariq S.R., Shah M.H., Shaheen N.. Khalique A., Manzoor S., And Jaffar M., (2005) Multivariate analysis of selected metals in tannery effluents and related soil, Journal of Hazardous Materials, 122, p. 17–22

Tornqvist R., Jarsjo J., And Karimov B., (2011) Health risks from large-scale water pollution: trends in Central Asia, Environment International, 37, p. 435–442

Treybal E.R., (1981) Mass Transfer Operations, McGraw-Hill International editions, Singapore

Tseng R.L., Tseng S.K., And Wu F.C., (2006) Preparation of high surface area carbons from corncob using KOH combined with CO_2 gasification for the adsorption of dyes and phenols from water, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 279, p. 69–78

Tunay O., Kabdasli I,. Orhon D., And Ates E., (1995) Characterization and pollution profile of leather tanning industry in Turkey, Water Science and Technology, 32, p. 1-9

UK red list substances., (1991) Environmental Protection (Prescribed Processes and Substances) Regulations (SI 1991/472)

UNEP: United States Environmental Protection Agency., (1991) Tanneries and the Environment; A technical guide to Reducing the Environmental Impact of Tanning Operations, Paris

US Environmental Protection Agency., (1999) Integrated risk information system (IRIS) on cadmium, National Centre for Environment Assessment, Office of Research and Development, Washington, DC

Valix M., Cheung W.H., And McKay G., (2004) Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption, Chemosphere, 56, p. 493–501

Verma A.K., Dash R.R., And Bhunia P., (2012). A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, Journal of Environmental Management, 93, p. 154–168

Wang S., (2008) A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, Dyes Pigments, 76, p. 714–720

Wei J.C., Liang P., Cao X.X., And Huang X., (2011) Use of inexpensive semicoke and activated carbon as biocathode in microbial fuel cells, Bioresource Technology, 102, p. 10431–10435

Whang T.J., Hsieh M.T., And Chen H.H., (2012) Visible-light photocatalytic degradation of methylene blue with laser-induced Ag/ZnO nanoparticles, Applied Surface Science, 258, p. 2796–2801.

World Bank., (1999) Tanning and leather finishing, In pollution prevention and abatement handbook, World Bank Group, Washington DC, p. 404

Wu J., Doan H., And Upreti S., (2008) Decolorization of aqueous textile reactive dye by ozone, Chemical Engineering Journal, 142, p. 156–160

Wu, F.C., And Tseng R.L., (2004) High adsorption capacity NaOH activated carbon for dye removal from aqueous solution, Journal of Hazardous Materials, 152, p. 1256–1267

Xu Y., And Lebrun R.E., (1999) Treatment of textile dye plant effluent by nanofiltration membrane, Separation Science and Technology, 34, p. 2501–2519

Yamashita J., Shioya M., Kikutani T., And Hashimoto T., (2001) Activated carbon fibers and films derived from poly (vinylidene fluoride), Carbon, 39, p. 207–214

Yan C., Wang C., Yao J., Zhang L., And Liu X., (2009) Adsorption of methylene blue on mesoporous carbons prepared using acid- and alkaline-treated zeolite X as the template, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 333, p. 115–119

References

Yewalkar S.N., Dhumal K.N., And Sainis J.K., (2007) Chromium reducing Chlorella sp. Isolated from disposal sites of paper-pulp and electroplating industry, Journal of Applied Phycology, 19, p. 459-465

Zhang F., Yediler A., Liang X.M., And Kattrup A., (2002) Ozonation of the purified hydrolyzed azo dye reactive red 120 (CI), Journal of Environmental Science & Health, 37, p. 707-713

Zhong Z.Y., Yang Q., Li X.M., Luo K., Liu Y., And Zeng G.M., (2012) Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption, Industrial Crops and Products, 37, p. 178– 185

APPENDICES

Appendix I

Comparison of Composite Metal Level in Tannery Effluent with NEQS

S. No	Metal	NEQS (mg/L)	Kasur (mg/L)
1	Cr	1.0	412.57
2	Cd	0.1	6.93
3	Zn	5.0	8.53
4	Ni	1.0	9.52
5	Pb	0.1	11.59

Appendix II

The Average Pollution Load in Tannery Effluents per Ton of Hides and Skin Processed

S. No	Pollution Parameter	Pollution Load (Kg)
1	BOD_5	70
2	COD	180
3	Chlorides	270
4	Dissolved Solids	600
5	Suspended Solids	100
6	Sulphides	4
7	Total chromium	30

Source:

Augustus T., (1996) The Pakistan Leather Industry (LEATHER), http://www.american .edu/project/mandala/TED/leatherhtm

Appendix III

National Environmental Quality Standards for Tannery Effluents

S. No	Parameter	Discharge Limit (mg/L)
1	Temperature	40 °C
2	pH	6-8
3	SO_4^{-2}	500
4	S^{-2}	1.0
5	Cl^-	500
6	Ca	100

Source:

National Environmental Quality Standards (NEQS)., (1999) Pakistan Environmental Protection Agency, Government of Pakistan