Removal of Chromium from Tannery Waste Water using Egg Shell as an Adsorbent

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B.Sc.(Hons.) in Chemistry, University of Dalanj(2003)

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Department of Chemical Engineering and Chemical Technology
Faculty of Engineering and Technology

May - 2017
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قال تعالى:

وَاللهُ جَعَلَ لَكُم مِّن بُيُوتِكُم سَكَنًا وَجَعَلَ لَكُم مِّن جُلُودِ الأَنْعَامِ بُيُوتًا تَسْتَخْفِفُوهَا لَيْوَمِ يَوْمِ الْعَدُوِّ وَيَوْمِ الْغُلُوِّ إِلَى حِينٍ صِدِّقُ اللَّهُ العَظِيمُ

(سورة النحل الآية 80)
Dedication

To my parents, my teachers, my son, and my colleagues, I dedicate this research ....
ACKNOWLEDGMENT

Firstly I specify my great thanks to Allah for his benefits, facilities, and properties which cover me, and then I want to thanks deeply Dr. Fathelrahman Abbas for his great help in all steps of this research in spite of his great responsibility, My great thanks to my co supervisor Dr. Mohamed Osman Babekir for his valuable discussion, suggestions and support.

Don't forget to thanks University of Gezira, Faculty of Engineering and Technology for giving me a chance for education. Lastly my thanks to everyone who; asked, encouraged, and gave me any help.
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ABSTRACT

Chromium is a heavy metal that is present in the environment in several different forms; the most common forms are chromium (III) and chromium (VI). The sources are waste water of electroplating, leather tanning, cement and paint industries. This study aimed at investigating the removal of chromium from tannery waste water by using eggshell as an adsorbent. The sample of waste water containing chromium was collected from Afrotan tannery – Albagger industrial area; in poly ethylene bottles and filtered by filter paper to remove solid residuals. Eggshells were collected from local restaurants in Alkalakla grounded, washed with deionized water, dried, sieved in different sizes (63, 125 and 250 μm) and kept in poly ethylene package for further work. The analyses were performed using chemical and instrumental methods. pH values are measured by pH meter. A known volume of waste water samples (50 ml) were transferred in a glass beakers and different concentrations of eggshell powders were added to each beaker then stirred by magnetic stirrer for different contact times. The beakers removed from magnetic stirrer and left to settle at room temperature then filtered. The concentration of chromium before and after treatment was determined by atomic absorption spectroscopy (AAS), to see the effect of the following parameters; contact time, size of adsorbent, pH of the sample and dose of adsorbent. The results obtained showed that the concentration of chromium before treatment was 0.419 ppm and the highest removal of chromium after treatment were 0.140 ppm at 30 minits contact time, at pH 8, 1 g of adsorbent and 63 μm adsorbent sizes. This indicates that eggshell is an effective and low cost adsorbent for the removal of chromium from tannery waste water. According to the results obtained from this study it is recommended that the eggshell be utilized for removal of chromium form waste water due to its effectiveness and low cost. Further studies on eggshell are needed to increase the efficiency at various conditions.
إزالة الكروم من مياه الصرف الصحي للدباغة باستخدام قشر البيض كمادة مازة

منتصر نصر بحر أبكر

ملخص الدراسة

الكروم هو معدن ثقيل يوجد في البيئة في عدة أشكال أكثرها شيوعاً هو الكروم (III) والكروم (VI). المصادر هي مياه الصرف الصحي الناتجة من الطلاء الكهربي، ودباغة الجلود، وصناعة الأسمنت والدهانات. هدفت هذه الدراسة إلى التعرف على إزالة الكروم من مياه الصرف الصحي للدباغة باستخدام قشر البيض كمادة مازة قليلة التكلفة. تم جمع عينات من مياه الصرف الصحي تحتوي على الكروم من مدبغة آفروتان - الباقر المنطقة الصناعية في زجاجات البولي إيثيلين وتم ترشيحها بواسطة ورق الترشيح لإزالة المخلفات الصلبة. تم جمع قشر البيض من المطاعم المحلية في منطقة الكلاكلة ثم غسله بالماء منزوع الأيونات وجفف ثم حفظه بأحجام مختلفة (1,250,1052) ميكرومتر في عبوات البولي إيثيلين لمزيد من الاستخدام. تم إجراء التحاليل بواسطة الأجهزة والطرق الكيميائية. حيث قيست قيم الأس الهيدروجيني بواسطة جهاز قياس الأس الهيدروجيني. تم نقل حجم معلوم من عينات لمياه الصرف الصحي 8 مل إلى كأسات زجاجية وأضيفت إليها مساحيق قشرة البيض بتركيزات مختلفة لكل كأس ثم خلطها بالخلاط المغناطيسي في أزمان إتصال مختلفة. تم إزالة الكاسات من الخلاط المغناطيسي وتركت تستقر عند درجة حرارة الغرفة ثم ترشيحها. تم تحديد تركيز الكروم قبل وبعد المعالجة بواسطة جهاز طيف الإصبع، لمعارفة تأثير العوامل الفيزيائية والكيميائية التالية : الزمن المتواصل وحجم المادة المازة والأس الهيدروجيني وكمية المادة المازة. وأظهرت النتائج أن تركيز الكروم قبل المعالجة كان 0.419 جزء في المليون، وأعلى إزالة لللكروم بعد المعالجة 0.140 جزء في المليون وذلك عند 30 دقيقة من الزمن المتواصل، الأس الهيدروجيني يساوي 8، كمية المادة المازة 1 جرام وحجم المادة المازة 63 ميكرومتر. وهذا يدل على أن قشر البيض يعتبر مادة فعالة وقليلة التكلفة لإزالة الكروم من مياه الصرف الصحي للدباغة. وفقًا للنتائج التي تم الحصول عليها في هذه الدراسة فيوصى أن تتم الاستفادة من قشر البيض لإزالة الكروم من مياه الصرف الصحي نظراً لفعاليته وقلة التكلفة. كما يوصى بالمزيد من الدراسات على قشر البيض لزيادة الكفاءة في ظروف مختلفة.
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Chapter One

Introduction
Chapter One

1. Introduction

1.1. Background:
Chromium is a heavy metal that’s present in the environment in several different forms; the most common forms are chromium (III) and chromium (VI) Ambasht, R.S(1983). The sources of chromium are waste waters of electroplating, leather tanning, cement, and paint industries. Chromium removal techniques such as precipitation, membrane techniques and solvent extraction are challenged by the removal of lower concentrations of metals from solution. On the other hand, adsorption has been proven to be one of the respective methods which are a simple, selective and economical process for the removal of heavy metal ions from aqueous solutions. Adsorption on smectite-rich clays, i.e. eggshell is a reliable method of metal removal owing to its simplicity, ion exchange and adsorption mechanisms due to its relative high cation exchange capacity (CEC) and specific surface are. Exposure of chromium can occur through the three major routes, via Absorption through the skin, by direct ingestion and by inhalation of chromium containing particles. The oral LD 50 of Na₂Cr₂O₇ (sodium chromate) in humans has been reported to be 50 ppm (NIOSH, 1992). The absorption of chromium is largely dependent on the oxidation state of the metal and the physical characteristics of the compound itself. Cr (VI) compounds can penetrate the skin more readily than trivalent forms, and uptake is enhanced with increases in the pH of the chromium containing substances. The absorbed Cr(VI) is quickly reduced to Cr(III), which binds strongly to the skin and its proteins. The absorption of Cr (VI) may be increased through broken skin or local actions (dermatitis), as occurs frequently with workers bearing chromium induced dermal ulcerations.

Some specific effects of higher blood levels of chromium include lung cancer, skin ulcers, brain damage, encephalopathy symptoms, and necrosis-localized death of a cell or cells in the living body tissues, pneumoconiosis—a lung disease caused by the inhalation of dust particles around the lungs, organoleptic problems, emphysema, bronchitis, and carcinoma. Chromium compounds are responsible for wide range of respiratory effects. Regarding carcinogenicity of chromium, several Cr⁶⁺ compounds like chromate are quite potent carcinogens. The incidence of lung cancer increases due to long term exposure to low to high levels of sodium chromate (Morton Lippman, 1991). Chromium (VI) has been found carcinogenic and is well documented by experiments with animals (Sujana, and Rao.1997). There is some evidence to establish that the
insoluble portion of chromium (VI) is more responsible for cancer incidence (Sujana, and Rao, 1997). Chromium (VI) in high dose has been implicated as the cause of digestive tract cancer. There is an increase in risk of lung cancer for workers, who are exposed to high levels of chromium. Chromium (VI) is highly corrosive and cause chronic ulceration of skin surfaces and perforation of the nasal septum. It has been reported that large doses of chromium (VI) in impure chromium compounds cause short term mutagenic damages (Timmy Kayla, 1979). In addition, the effects of chromium (VI) are the causative factor through easy reducibility of chromium (VI) by organic tissues in the body. The size of chromium (VI) ion radius is in the range as the perforation size in human cell walls. After entering the cells, the ion is reduced to chromium (VI). Since, chromium (III) being higher radius is retained in cell walls. These degenerative responses occur rapidly and are dependent of the dose and any hypersensitivity reactions. Physiological disorders arising out due to prolonged exposure of chromium (III) have been reported (Morton Lippman, 1991). Cases of acute systemic poisoning are rare; however, they may follow deliberate or accidental ingestion. Chromium poisoning effects include skin disorders, liver damage, gastric distress, olfactory sense impairment, nosebleeds and yellowing of the tongue and teeth. The tetrogenicity of chromium (III) has been demonstrated in animal studies (Morton Lippman, 1991). These include malformations and open eyelids as well as increased evidence of skeletal defects. Genotoxicity and mutagenicity occur due to chromium (VI) and chromium (III). This is powerful in most prokaryotic and eukaryotic cell systems. The lethal oral dose for soluble chromium compound is considered to be 50-ppm bodyweight. Short duration exposures to air borne, liquid or solid chromium compounds lead to the clinical symptoms of acute toxicity on human which are vomiting, diarrhea, hemorrhagic diathesis and blood loss into the gastrointestinal tract causing cardio vascular shock. Other diseases are allergic contact dermatitis, skin ulcers, nasal membrane inflammation, nasal ulceration, glycosuria, liver, necrosis, nephritis, aortic plaque atherosclerosis, serum albumin, globulin, necrosis and desquamation of the epitheliums in the kidney, diarrhea, cyanosis, tail necrosis and gastric ulcers (Morton Lippman, 1991). Prolonged exposure to airborne or solid, liquid chromium compounds lead to chronic toxic effects on humans. The diseases are nasal septum perforations, ulceration's of skin surfaces, rhinitis, liver damage, pulmonary congestion, edema, nephritis, intestinal lung and gastric cancers, irritation of gastrointestinal mucosa, chronic total parental nutrition, (Symptoms like weight loss, hypoglycemia), respiratory effects, congestion and hyperemia,
Chronic rhinitis, congestion and hyperemia, chronic rhinitis, congestion of larynx polyps of the upper respiratory tract, inflammation of lungs, emphysema, bronchitis, bronchopneumonia, lung tumors, malignant tumor, coetaneous and nasal mucous, membrane ulcers (Morton Lippman, 1991). Because chromium can be used for many purposes, there is the potential for exposure in a variety of industries. The risk of exposure is through inhalation of chromium bearing aerosols. Additionally, there are wide variations in the possible aerosol characteristics such as the relative proportions of the major oxidation states of the chromium bearing particles as well as varying solubility within these fractions. Chromium (VI) is readily absorbed from the respiratory system, whereas chromium (III) is not. Under normal exposure conditions (that are atmospheric chromium), absorption of chromium from the respiratory tract has been estimated to be less than 1 g/day. Absorption from the lung is dependent on the characteristics of the aerosol, including the size, shape, hygroscopicity, and over all electric charge of chromium containing particles. Other factors that may influence the absorption of these particles include ambient temperature, solubility in body fluids and reactions with other air-borne agents. In the gastrointestinal tract, only 1% of an ingested dose of chromium (III) is absorbed, whereas absorption of chromium (VI) is 3-6%. The poor absorption of the chromium (VI) may be related to its rapid reduction to the trivalent form by components of saliva and gastric juice. Once chromium has entered the bloodstream, it is reduced to chromium (VI) by components normally present in the blood such as ascorbic acid and glutathione. The oxidation state of chromium is the determining factor for its transportation via the bloodstream. Chromium (VI) is mainly transported via the serum, bound to the iron-binding transferring and β-globulin fraction of serum proteins; however at high concentrations chromium (III) binds to serum albumin or α1- or α2-globulin. In contrast to chromium (III), chromium (VI) can readily cross the erythrocyte membrane and bind to the globulin portion of hemoglobin following oxidation of the heme group (Morton Lippman, 1991). Inside these cells, chromium (VI) is reduced to chromium (III) by glutathione and then becomes trapped intracellularly. Consequently, the degradation products of erythrocytes may explain, in part the high concentration of chromium found in the spleen and the slow excretion of chromium from the body. The genotoxicity of chromium compounds has been documented (Kirthothmer, 1960). The chromium (VI) ion is readily taken up into eukaryotic cells by anion-carrying proteins, after which it is reduced to chromium (III) by a number of cytoplasm reducing agents. The final cellular for of chromium (III) becomes trapped
intracellular because it has low cell membrane permeability. This shift from chromium (VI) to chromium (III) allows a concentration gradient to be established such that a continual influx of chromium (III) ions raises intracellular chromium levels until the metal burdens become lethal. Most chromium (VI) salts were mutagenic and chromium (III) salts are relatively non-mutagenic. Chromium to be capable of inducing chromosomal aberrations and enhancing cells transformation. Although both the valence states of chromium are able to interact with DNA, chromium (III) ions are responsible for decreasing the fidelity of DNA replication. In addition, both chromium (III) and chromium (VI) exhibit a clastogenic potency; however, chromium (VI) possesses the greater activity and is powerful mutagen in many prokaryotic and eukaryotic cell systems. These properties chromium (VI) of support the claim that chromium (VI) compounds are likely to be active carcinogens, although it is more likely that the ultimate species responsible for the carcinogenic/mutagenic effects observed in vivo is the intracellularly derived chromium (III) form (Winslow, H. 1972). Particulate from coal-fired power plants has been shown to contain chromium in the range of 2.3-31 ppm; however, these levels are reduced to 0.19-6.6 ppm by fly ash collection processes. Chromium in ambient air originates from industrial source (that is steel manufacturing and cement production) and the combustion of fossil fuels; the content in coal and crude oil varies from 1-100 μg/l and 0.005 to 0.7 μg/l respectively. In rural areas, chromium levels in the air are usually less than 10-ng/m³ whereas the concentration varies from 10-50 ng/m³ in industrial cities (James, M. Sontag, 1986). Epidemiological studies of the incidence of cancer in occupationally exposed individuals have indicated that cancer mortality rates in the workers were 5-40 times higher than expected. An excess incidence of lung cancer shad been reported in workers in the chromate plants. Cancer of the nasal cavities as well as of the larynx is reported in a small exposure population. A survey of chromate plants showed an increased risk of cancer in two of the plants (Probability of 0.66). An increased gastric cancer has been observed among metal finishers. There were five incidences instead of three cases expected (Morton Lippman, 1991). Overwhelming epidemiological evidence shows a considerable excess of chromium compounds-induced occupational cancers, with a pre-dislocation to the lung, nasal cavity, sinuses, and larynx. It is found that 70% of the cases had lent periods between 11 and 30 years. The distribution of compounds containing chromium(III) and chromium(VI) depends on the redox potential, the pH, the presence of oxidizing or reducing compounds, the kinetics of the
redox reactions, the formation of chromium(III) complexes or insoluble chromium(III) salts, and the total chromium concentration. In the environment, chromium (VI) occurs mostly as \(\text{CrO}_4^{2-}\) or \(\text{HCrO}_4^-\) and chromium (III) as \(\text{Cr(OH)}_n(3-n)^+\). In soil, chromium (III) predominates. Chromium (VI) can easily be reduced to chromium (III) by organic matter, for example, and its occurrence in soil is often the result of human activities. In water, chromium (III) is a positive ion that forms hydroxides and complexes, and is adsorbed at relatively high pH values. In surface waters, the ratio of chromium (III) to chromium (VI) varies widely, and relatively high concentrations of the latter can be found locally. In general, chromium (VI) salts are more soluble than those of chromium (III), making chromium (VI) relatively mobile. In air, chromium is present in the form of aerosols. It can be removed from the atmosphere by wet and dry deposition. Both trivalent and hexavalent chromium are released into the air. Because of analytical difficulties, data on chromium speciation in ambient air are rarely available, but the proportion present as chromium (VI) has been estimated as 0.01–30%, based on one study. The leather dust is the carrier of chromium in all its forms and makes it mobile and dangerous. The fine leather dust whose size varies from less than one micron to higher values is easily absorbed through skin and is inhaled. The fibres are usually from 10 to 120 microns in length and 0.5 to 50 microns in diameter. It is of insidious nature and fibrous minute particles being powdered during the Ginning process report to cause lung cancer, mesothelioma, chest pain, cough and asthma (Rao, M.N., 1995). Several studies have shown that chromium (VI) compounds can increase the risk of lung cancer. Animal studies have also shown an increased risk of cancer. The World Health Organization (WHO) has determined that chromium (VI) is a human carcinogen. The Department of Health and Human Services (DHHS) has determined that certain chromium (VI) compounds are known to cause cancer in humans.

Chromium (III) is an essential nutrient that helps the body use sugar, protein, and fat. Breathing high levels of chromium (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage and even death. The most common health problem in workers exposed to chromium involves the respiratory tract. These health effects include irritation of the lining of the nose, runny nose, and breathing problems (asthma, cough, shortness of breath, wheezing). Workers have also developed allergies to chromium compounds, which can cause breathing difficulties and skin rashes. The
concentrations of chromium in air that can cause these effects may be different for different types of chromium compounds, with effects occurring at much lower concentrations for chromium (VI) compared to chromium (III). However, the concentrations causing respiratory problems in workers are at least 60 times higher than levels normally found in the environment. Respiratory tract problems similar to those observed in workers have been seen in animals exposed to chromium in air (Odum. 1971).

1.2. Structure and composition of eggshell and membrane:
The eggshell which forms the outer crust of an avian egg is a natural porous bioceramic, which has largely been studied since 1964. The structure of the eggshell and membrane is now very well understood due to scanning electron microscopy and microfocus X-ray scattering techniques (Lammie et al. 2005). However, ambiguities regarding its composition still exist.
The eggshell which consists of various different layers can be described as a well organized structure, the formation of which begins at different segments of the hen’s oviduct. A number of different proteins (soluble and insoluble) and minerals are deposited during the process of eggshell formation which is later used up by the developing embryo. The insoluble proteins have been suggested to act as structural framework and the soluble proteins become embedded in the calcified layers. The deposited mobilized calcium is used for the development and formation of embryo’s skeleton (Lammie et al. 2005; Stadelman and Cotterill 1996).
The eggshell which is largely made up of calcium carbonate (95%) and minor amount of organic matrix (3.5%) (Nys and Gautron 2007) can be divided into six different layers (inside to outside). The inner shell membrane forms the innermost layer (20 μm thick) and is in direct contact with the albumen. The outer membrane which lies just above the inner membrane is approximately 50 μm thick. Both, the inner membrane and the outer membrane are made up of interwoven protein fibers and lie parallel to the egg surface providing structural support to the eggshell as a whole (Lammie et al. 2005; Nys and Gautron 2007). The shell membranes greatly influence the shell strength and also prevent micro-organism penetration. The proteins of the shell membranes have been found to have a high content of arginine, cystine, glutamic acid, histidine, methionine and proline (Stadelman and Cotterill 1996).
The calcified portion (consisting of calcium carbonate crystals) of the shell which precedes the outer membrane can be divided into three layers; the mammillary layer, palisade layer and the vertical crystal layer (Lammie et al. 2005).
The mammillary layer (70 μm thick) which forms the inner most layer of the calcified portion of the eggshell penetrates the outer membrane by means of numerous carbonate cones. The initiation of the formation of calcium carbonate crystals takes place at the mammillary knobs, which are organic cores deposited during the egg formation (Lammie et al. 2005).

The palisade layer (200 μm thick) lies above the mammillary layer and forms the major portion of the calcified layer of the eggshell. In this layer the calcite crystals grow perpendicular to the eggshell membranes. It also has a small portion (2-5%) of organic matrix incorporated in the calcite crystals. Pores formed in the palisade layer help in the exchange of gases. The formation of pores takes place when the adjacent crystals fail to fully join each other along their side surfaces, leaving a gap between the crystals. The palisade layer gives way to the vertical crystal layer (Lammie et al. 2005; Stadelman and Cotterill 1996; Nys and Gautron 2007).

The vertical crystal layer which is about 8 μm thick is a very narrow/thin layer and consists of the upper most part of calcite crystals which provides a surface for the formation of the cuticle (Lammie et al. 2005; Nys and Gautron 2007).

The cuticle is the outer most water insoluble layer of the eggshell (10 – 30 μm thick) (Lammie et al. 2005; Nys and Gautron 2007). The layer is largely an organic layer with protein contents as high as 90% and with a high content of cystine, glycine, glutamic acid, lysine and tyrosine. Fucose, galactose, glucose, hexosamines, mannose, and sialic acid have been reported to be present as constituents of the polysaccharides (Stadelman and Cotterill 1996). The calcified portion (consisting of calcium carbonate crystals) of the shell which precedes the outer membrane can be divided into three layers; the mammillary layer, palisade layer and the vertical crystal layer (Lammie et al. 2005).

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surfaces, leaving a gap between the crystals. The palisade layer gives way to the vertical crystal layer (Lammie et al. 2005; Stadelman and Cotterill 1996; Nys and Gautron 2007).

The vertical crystal layer which is about 8 μm thick is a very narrow/thin layer and consists of the upper most part of calcite crystals which provides a surface for the formation of the cuticle (Lammie et al. 2005; Nys and Gautron 2007).

The cuticle is the outer most water insoluble layer of the eggshell (10 – 30 μm thick) (Lammie et al. 2005; Nys and Gautron 2007). The layer is largely an organic layer with protein contents as high as 90% and with a high content of cystine, glycine, glutamic acid, lysine and tyrosine. Fucose, galactose, glucose, hexosamines, mannose, and sialic acid have been reported to be present as constituents of the polysaccharides (Stadelman and Cotterill 1996).

1,3. Instrumental technique:

In choosing the most appropriate analytical method to determine metals, each laboratory must consider the sample types and the concentration levels, the number of elements to be determined and the costs. As a result, flame and graphite furnace atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP and ICP – MS) emission spectrometry are the most widely used analytical methods for determining trace elements

1,3,1. Atomic absorption process:

The quantity of interest in atomic absorption measurements is the amount of light of the resonant wavelength which is absorbed as the light passes through a cloud of atoms. As the numbers of atoms in the light path increases, the amount of light absorbed, increases in a predictable way. By measuring the amount of light absorbed, a quantitative determination of the amount of the analyte element can be made. The use of special light sources and careful selection of wavelength allow the specific quantitative determination of individual element in the presence of others. The atom cloud required for atomic absorption measurements is produced by supplying enough thermal energy to the sample to dissociate chemical compounds in to free atoms. Aspirating a solution of the sample in to a flame aligned in the light beam serves this purpose. Under the proper flame conditions, most of the atoms will remain in the ground state form and are capable of absorbing light at the analytical wavelength from a source lamp. The ease and
speed at which precise and accurate determinations can be made with this technique have made atomic absorption one of the most popular methods for determination of metals (Harvey, 2008).

Atomic absorption using either flame or electro thermal atomization is widely used for the analysis of trace metals in a variety of sample matrices. Using the atomic absorption analysis of zinc as an example, procedures have been developed for its determination in samples as diverse as water and waste water, air, blood, urine, tissue, hair, milk, breakfast cereals, shampoos, alloys, industrial plating baths, gasoline, oil, sediment and rocks.

Developing a quantitative atomic absorption method require several considerations, including choosing a method of atomization, selecting the wavelength and slit width, preparing the sample for analysis, minimizing spectral and chemical interferences and selecting a method of standardization (Beaty and Kerber, 1993).

Basic components, every absorption spectrometer must have components, which fulfill the three basic requirements shown in the following figure. There must be:

1- alight source 2- a sample cell; and 3- a specific light measurement.

Figure1: components of AAS
1.4. Objective of the study:

The main objective of this study is the investigation of the effect of size of the adsorbent, pH, contact time and adsorbent concentration on adsorption of chromium from the tannery waste water using eggshell as an adsorbent.
Chapter Two
Literature Review
Chapter Two

2. Literature Review

2.1. An Over view:
Several low cost biomaterials such as rice husk, sugar cane bagasse, Tulsi Leaf & branches, coconut shell & coir and fly ash were tested for removal of chromium; all the experiments were carried out in batch process; the results obtained showed that the Tulsi leaf do not give fruitful result (23.340 % Removal); So, it is advice not to use Tulsi leaf as an adsorbent for removal of hexavalent chromium; Coconut Shell gives better result (81.999% removal) in comparison of other agricultural waste material (Prashant and Gupta, 2014). However rice husk, saw dust and eucalyptus bark (EB) were tested for removal of chromium; All the experiments were carried out in batch process with real effluents collected from several industries; The adsorbent, which had highest chromium (VI) removal was EB; Influences of chromium concentration, contact time on removal of chromium from effluent was investigated; The results indicated that eucalyptus bark can be used for the removal of chromium (Xavier et al. 2013). Chitosan-charcoal composite was applied as a media to treat tannery effluent. The composite was prepared by a simple solution-evaporation method and the morphology of the prepared composite was characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Adsorption of chromium (Cr) was investigated by varying the contact time between adsorbate (Cr) and composite, pH of solution and dose of composite. The concentration of Cr was determined by atomic absorption spectroscopy (AAS). Removal of Cr was found to be dependent on pH and maximum adsorption was observed at pH 4.0. The optimum dose and contact time for Cr treatment was 40 g/L and 250 minutes respectively. The results showed that prepared composite can be used efficiently for the treatment of tannery wastewater containing chromium (Shajahan et al. 2012).

The activated carbon produced from olive stones was chemically activated using sulfuric acid, (OS-S), and utilized as an adsorbent for the removal of Cr (VI) from aqueous solution in the concentration range 4-50 mg/L. Adsorption experiments were carried out in a batch process and various experimental parameters such as effect of contact time, initial chromium ion concentration, carbon dosage, and pH on percentage removal have been studied. Adsorption
results obtained for activated carbon (OS-S) were compared with the acid-treated commercial activated carbon (CAC-S). The optimum efficiency shows that the Cr (VI) uptake being attained at pH 1.5. The equilibrium adsorption data was better fitted to the Langmuir adsorption model. The results of kinetic models showed that the pseudo-first-order kinetic model was found to correlate the experimental data well. It was concluded that activated carbon produced from olive stones (OSS) has an efficient adsorption capacity compared to (CAC-S) sample (Attia et al. 2010).

Sheikh and Viqar (2013) investigated the low cost-effective approach of removing chromium (VI) from fifteen different samples of tannery effluents collected from the city of Kasur by using bio-sorbent wheat bran; Tannery effluents samples were treated with Wheat Bran (WB); after adsorbent treatment, filtrate was analyzed for the concentration of chromium ions using a UV-Visible Spectrophotometer at 540 nm; The batch system was used to conduct the bio-sorption experiments; The influence of different experimental parameters, such as contact time, pH, amount of adsorbent, was evaluated. Results showed that adsorption of chromium (VI) by wheat bran reached to maximum after 240 minutes; higher chromium (VI) adsorption was determined at pH 3; Results obtained from the present study were in accordance to international studies. Efficiency evaluation of non-conventional low cost adsorbents such as Fly ash powder, Bagasse, W.Straw Dust, SD, and Coconut coir as compared to the powder activated carbon for the removal of chromium from aqueous solution were conducted; The efficiency of the adsorbents for the removal of chromium was investigated; The effect of chromium solution pH, contact time, adsorbent dosage, initial chromium concentration and adsorbent meshsize on adsorption were studied in a batch experiment. Fly ash, Bagasse, W.S.D, SD, &Coconut coir were the most active at pH-6, which is closer to pH of chromium bearing industrial waste as compared to the pH 2.0 of PAC; The ultimate adsorption capacity for the adsorbents PAC, Bagasse,FA, S.D., W.S.D & Coconut coir found out are 4.97 mg/gm, 4.91mg/gm, 4.90mg/gm, 4.89 mg/gm, 4.77mg/gm and 4.56 mg/gm respectively by column studies(Talokar, 2011).

The removal of chromium from industrial effluents and from wastewater using egg shell, were studied. Experimental results demonstrated that this extraction method was found to be cheaper, quicker and more efficient than other conventional techniques (Rajendran and Mansiya 2011). Investigation of low cost activated sugar cane bagasse for effective removal of hexavalent chrome from aqueous solutions conducted by Nigus Gabbiye Habtu et al.; the bagasse was
collected from different sites of Gondar town, Ethiopia by plastic bags. To increase surface porosity, sugar cane bagasse was pretreated with sulfuric acid. The adsorbent was characterized by FT-IR spectrometry and Sear method for its surface chemistry and BET surface area respectively. The effect of initial concentration, adsorbent dose, pH, contact time and temperature on the batch adsorption/desorption process were examined. The result obtained indicates that pH 1 is found to be the optimal pH for effective removal of Cr (VI) over activated carbon derived from bagasse. Over 99.0 % removal efficiency was achieved with the acid treated activated carbon. It was found also that the Cr (VI) removal was increased with the increment of the adsorbent dosage and contact time. A result of 78.8% Cr (VI) recovered was achieved at basic media. The possibility of the adsorbent regeneration were based on the general assumptions that desorption promotes economic adsorption treatment. Generally, this study demonstrates that acid treated bagasse is an effective and cheap adsorbent for the removal of Cr (VI) from solution of leather industrial wastes (Nigus Gabbiye Habtu et al. 2014).
Chapter Three
Materials and Methods
Chapter Three
3. Materials and Methods

3.1. Materials:

3.1.1. Sampling:

Effluents wastewater containing chromium was collected from Elbagair tannery. The samples were collected in polythene bottles and filtrated by filter paper to remove solid residuals; then subjected to analysis by atomic absorption spectroscopy for determination of chromium quantity in the effluents.

3.1.2. Preparation of the adsorbent:

In this study eggshell was used as an adsorbent, which collected from kitchen and restaurants as waste material; then grounded, washed with deionized water, dried, sieved in different sizes (63, 125 and 250 µm) and kept in polythene packages for further working.

3.1.3. Reagents

All chemicals used in this study were analytical grade; they were bought from local market and used without further purification.

3.1.4. Preparation of 0.1M Sodium Hydroxide Solution:

4.0 g of sodium hydroxide were dissolved in a glass beaker with small quantity of distilled water; then quantitatively transferred to 1 liter volumetric flask and then filled with distilled water up to the mark.

3.1.5. Preparation of 1:1 Hydrochloric acid Solution:

500 ml of concentrated HCL solution was transferred in to a 1000 ml volumetric flask and then the solution completed with distilled water up to the mark.

3.2.1. Sample treatment:
- **Influence of adsorbent size**
  Three glass beakers in each one a 50 ml of wastewater were added, 1.0 g of adsorbent of different sizes: 63,125 and 250 μm were added into each glass beaker, and then the solution stirred magnetically for 30 mints, kept at room temperature for a time and then filtered. The concentration of chromium in the treated sample solutions were determined by AAS.

- **Influence of pH**
  1.0g of adsorbent was dissolved in glass beaker with 50.0 ml of water sample, the solution stirred by magnetic stirrer for 30 mints the beaker removed from magnetic stirrer and kept at room temperature for a time and then filtered, the concentration of chromium in the treated sample solution was determined by AAS.

  1.0g of adsorbent was dissolved in glass beaker with 50.0 ml of water sample and 5.0 ml of 0.1M sodium hydroxide was added to the solution and stirred for 30mints by magnetic stirrer, the beaker removed from the magnetic stirrer and kept at room temperature for a time and then filtered, finally the concentration of chromium in the treated sample solution was determined by AAS.

  1.0g of the adsorbent was dissolved in glass beaker with 50.0 ml of water sample and 10.0 ml of 0.1 M sodium hydroxide, the solution was stirred for 30 mints by magnetic stirrer the beaker removed from the magnetic stirrer and kept at room temperature for a time then filtered and the concentration of chromium in treated sample solution was determined by AAS.

- **Influence of adsorbent quantity**
  Three sample solutions (A, B, C) treated by dissolving (1.0, 1.5 and 2.0) g of adsorbent respectively in three glass beakers each of them contain 50.0 ml of water sample, the solutions were stirred for 30 mints by magnetic stirrer, the beakers removed from the magnetic stirrer and kept at room temperature for a time and filtrated and then the chromium concentration in the treated sample solutions were determined by AAS.

- **Influence of contact time**
  Three sample solutions were treated by dissolving 1.0 g of adsorbent in each glass beaker which contain 50.0 ml of water sample, the solutions stirred for three different time (30, 45, and 60) mints by magnetic stirrer, after that the beakers removed from the magnetic stirrer
and kept at room temperature for a time, filtered and the chromium concentration in the treated sample solutions were determined by AAS.

3.2.2. Preparation of chromium standard solutions:

For the AAS analysis of treated samples standard solution of chromium were prepared by dissolve a 1.000 g of chromium metal in 1:1 hydrochloric acid with gentle heating. Cooled and diluted to one liter to give 1000 µg/ml Cr; and then five standard solutions (2.0, 4.0, 6.0, 8.0 and 10.0 ppm) were prepared from stock solution according to equation:

\[ C_1 V_1 = C_2 V_2 \]

![Fig 2: Calibration curve of chromium standard](image)

3.2.3. Apparatus and glass ware:

- Test tubes
- Calendar measurement
- Volumetric flasks
- Funnel
- Bottles
- Beakers
- Filter papers
- Conical flasks
3.2.4. Instruments:

- Magnetic stirrer (IKA C-MAGHSA)
- Atomic absorption spectrometer (55 AA Agilent Technologies)
- Sensitive Balance (Adventurer Made for OHAUS Corp- USA)
- pH Meter (HANNA pH 211 Microprocessor pH Meter)
Chapter Four
Results and Discussion
Chapter Four

4. Results and Discussion

4.1. Results:

Table 4.1.1: Shows the effect of particle size of the adsorbent on percentage of adsorption. It is clear that size 63 µm gave the highest percentage of adsorption and chosen for further investigations.

<table>
<thead>
<tr>
<th>NO</th>
<th>Size of adsorbent µm</th>
<th>Initial [Cr] by ppm(X)</th>
<th>Remaining [Cr] by ppm(Y)</th>
<th>[Cr] ads.ppm (X-Y)</th>
<th>[Cr] ads. % (X-Y/X)x100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63</td>
<td>0.419</td>
<td>0.236</td>
<td>0.183</td>
<td>43.675</td>
</tr>
<tr>
<td>2</td>
<td>125</td>
<td>0.419</td>
<td>0.268</td>
<td>0.151</td>
<td>36.038</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>0.419</td>
<td>0.275</td>
<td>0.144</td>
<td>34.367</td>
</tr>
</tbody>
</table>

Table 4.1.2: Shows the effect of pH on the percentage of adsorption. The pH was increased from 5-8 by adding NaOH solution. It is clear that with increasing the pH the percentage of adsorption increased.

<table>
<thead>
<tr>
<th>No</th>
<th>pH of the sample</th>
<th>Initial [Cr] by ppm (X)</th>
<th>Remaining [Cr] by ppm (Y)</th>
<th>[Cr] ads.ppm (X-Y)</th>
<th>[Cr] ads. % (X-Y/X)x100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.00</td>
<td>0.419</td>
<td>0.236</td>
<td>0.183</td>
<td>43.675</td>
</tr>
<tr>
<td>2</td>
<td>7.00</td>
<td>0.419</td>
<td>0.170</td>
<td>0.249</td>
<td>59.427</td>
</tr>
<tr>
<td>3</td>
<td>8.00</td>
<td>0.419</td>
<td>0.140</td>
<td>0.279</td>
<td>66.587</td>
</tr>
</tbody>
</table>

Table 4.1.3: Shows the effect of adsorbent concentration on percentage of adsorption. It is clear the percentage of adsorption increased with increasing adsorbent concentration.
Table 4,1,4. Shows the effect of contact time of the percentage of adsorption. An increase in the percentage of was observed with increasing adsorbent concentration.

<table>
<thead>
<tr>
<th>No</th>
<th>Time/ mints</th>
<th>Initial [Cr]/ppm (X)</th>
<th>Remaining[Cr]/ppm (Y)</th>
<th>[Cr] ads/ppm (X-Y)</th>
<th>[Cr] ads/% [X-Y/X]x100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>0.419</td>
<td>0.283</td>
<td>0.136</td>
<td>32.458</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>0.419</td>
<td>0.265</td>
<td>0.154</td>
<td>36.754</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>0.419</td>
<td>0.228</td>
<td>0.191</td>
<td>54.584</td>
</tr>
</tbody>
</table>

4,2. Discussion:

4,2.1. Factors influencing the adsorption of chromium by eggshell

Effect of size of adsorbent

The influence of size of the adsorbent on the chromium adsorption was studied by carrying out the experiment at various sizes 63, 125 and 250μm. The maximum adsorption was found to be at the size 63μm (as shown in table 1)

This can be attributed to the fact that as the size of the adsorbent decreases, the surface area of the adsorbent increases thereby increasing the extent of adsorption.
Effect of pH:
PpH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate. To examine the effect of pH on the chromium removal efficiency, the pH of chromium solution was varied from 5.0 to 8.0.

As shown in table 2. The uptake of free ionic chromium depended on pH, the Optimum metal removal efficiency occurred at pH 8.0.

Effect of dose:
The dependence of chromium adsorption on dose was studied by varying the amount of adsorbents from (1.000, 1.500 and 2.000) g by keeping the other parameters (pH, contact time) constant. From table 3 it could be observed that removal efficiency of the adsorbent generally increased with increasing dose. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions.

Effect of contact time:
The interaction of adsorbent and chromium contained solution was performed at pH 5.0 and adsorbent dose was 1.0g The contact time for treatment was varied from 30 min to 60min after centrifuging time for 15 min table 4 represents that removal efficiency increases with an increase in contact time. It can be seen that chromium removal efficiency of eggshell increased when Contact time was increased from 30 to 60 min. Optimum contact time for the adsorbent was found to be 60 min.
Chapter Five

Conclusion and Recommendations
Chapter Five

5. Conclusion and Recommendations

5.1. Conclusion:

The emission of large amount of neutral salt containing a high concentration of chromium in tanning wastewater will seriously affect the ecological environment. A cheap and convenient process for the removal of chromium from its aqueous solution has been studied in this present investigation by the use of, low cost adsorbent material, eggshell, which is commonly available and economically feasible. The process of removal was found to be effected by the dose of the adsorbent, size of adsorbent, pH and contact time. The concentration of chromium after treatment determined by atomic absorption method, the result obtained showed that the optimum condition for removal of chromium from tannery wastewater were 60 minutes contact time, pH 8.0, 2g of adsorbent and 63 µm adsorbent size. Based on the result chromium removal using egg shell is the best-suited technology in present context to clean up Chromium contaminated waste water as it is eco-friendly and cost effective.

5.2. Recommendations:

According to the results obtained from this study it is recommended that the eggshell could be utilized for removal of chromium form waste water due to its effectiveness and low cost. Further studies on eggshell are needed to increase the efficiency at various conditions.
References


19- Timmy Katyal,(1979) ( www.research gate.net),22/10/2016, 17 GTM