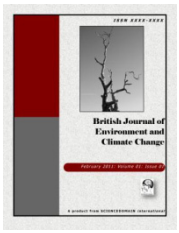

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Extraction of Chromium from Tannery Effluents Using Waste Egg Shell Material as an Adsorbent

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ABSTRACT

In the present era, due to industrial revolution in the developing country like India, the ground water system has been largely polluted, especially with heavy metals like chromium. The removal of such heavy metals from industrial effluents and from wastewater has become a subject of keen interest. This paper deals with the removal of chromium from its aqueous solution using egg shell, a waste material as an adsorbent. Experimental results vividly demonstrate that this extraction method was found to be cheaper, quicker and more efficient than other conventional techniques. The results are interpreted in the light of Loggergren's model.

Keywords: Heavy metal; chromium; egg shell; adsorption dynamics; Loggergren's model;

1. INTRODUCTION

Heavy metal pollution can affect all environment but its effects are most long lasting in soils because of the relatively strong adsorption of many metals onto the humid and clay colloids in soils. Unlike organic pollutants, which will ultimately be decomposed, metals will remain as metal atoms, although their separation may change with time as the organic molecules binding them decompose or soil conditions change (Trivedi and Goel, 1984). All metals are most soluble and bio-available at low pH and therefore, toxicity problems are likely to be more severe in acid environments.

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Tannery effluent is a major source of aquatic pollution in India with high chemical oxygen demand (COD), biological oxygen demand (BOD), and hexavalent chromium. There are a large number of tanneries scattered all over India. But the main areas of their concentration are Tamilnadu, Uttar Pradesh and West Bengal. Chromium, a steel-grey, lustrous, hard and brittle metal, occurs in nature in bound forms that constitute 0.1–0.3 mg kg-1 of the Earth's crust. It has several oxidation states ranging from Cr (-II) to Cr (+VI), the trivalent and hexavalent states are the most stable ones. A maximum acceptable concentration of 0.05 mg/L *(50* µ*g* / L*)* for chromium in drinking water has been established on the basis of health considerations (Natarajan, 1983).

Hexavalent chromium [Cr (VI)] compounds are being used in a wide variety of commercial processes and unregulated disposal of the chromium containing effluent has led to the contamination of soil, sediment, surface and ground waters. In trace amounts, chromium is considered an essential nutrient for numerous organisms, but at higher level, it is toxic and mutagenic. Nearly 80% of the tanneries in India are engaged in the chrome tanning processes. Most of them discharge untreated wastewater into the environment. In such aqueous waste, Cr (VI) is present as either dichromate ($Cr_2O_7^{2-}$) in acidic environments or as chromate (CrO_4^-) in alkaline environments. Chromium compounds were employed in textile coloring and leather tanning processes. The principal chromium emissions into surface waters are from metal finishing processes such as electroplating, pickling and bright dipping (Rajendran, 2010). Pollution of soils occurs as a result of the dumping of chromate wastes such as those from tanneries or electroplating and from sewage sludge disposal on land (Ambasht, 1983). Uncontrolled emissions have greater potential for contaminating the fresh waters with relatively toxic form of Cr (VI), which exist only as oxy species and is strongly oxidizing other small discharges of Cr (VI) are from the additive in circulating waters, laundry chemicals (Anandakrishnanadar et al., 1992). Sources of Cr (III) contamination include liquid waste discharges from leather tanning and textile dyeing containing up to several thousand mg/l of chromium. Municipal wastewaters release considerable amounts of chromium into the environment. However, the relatively more toxic chromium (VI) constituted less than 1 percent of the total chromium in the water. Toxicity of chromium (III) and chromium (VI) to aquatic organisms is generally low and chromium is not actually toxic to humans. However, Cr (VI) is more toxic than Cr(III),thereby reducing the toxic impact of chromium discharges, the stomach acidity reduces Cr(VI) to the much less toxic Cr(III) from whose gastrointestinal adsorption is less than1 per cent. Chromium (VI) can be carcinogenic, causing cancer of the respiratory organs in chromate workers chronically exposed to chromium containing dusts (Odum, 1971).

A number of methods are available to remove heavy metals from aqueous solutions. These methods have been used for the treatment of industrial wastes to remove Cr (III) and Cr (VI). These include neutralization, cementation, sulphide precipitation, hydroxide precipitation, flocculation-classification, sand–filtration, precipitation, ion exchange, and evaporative recovery process and sorption techniques (Rao and Datta, 1987). The people in Tamil Nadu, India especially Trichy and Karur are afflicted with water-borne diseases which are mainly attributed to the contamination of tannery effluents with drinking water bodies. These effluents due to insufficient removal of toxic metals like chromium discharge them in the nearby water systems. Physiological properties of chromium have been well documented. Trichy is an industrial area, where a large number of small-scale industries are located. These industries pollute the nearby soil and ground water with chromium as a heavy metal. In the present investigation, to estimate the amount of chromium ions present in its aqueous solutions before and after treatment and the removal of chromium from wastewater using eggshell as an adsorbent is attempted. Though many conventional adsorbent (Timberal,

1979). are used for the effective removal of heavy metal ions, egg shell has been chosen as adsorbents as they are thrown as kitchen waste materials from hotels, restaurants and hostels of schools and colleges with an aim to use waste/ pollutant material as adsorbent. The present work is also aimed at fixing the optimal conditions such as adsorbent size, pH, equilibrium time (for batch mode technique) etc., for effective removal of chromium.

2. EXPERIMENTAL DETAILS

2.1 Reagents

All the chemicals used in the investigation were Analar grade. They were used without further purification unless specified otherwise.

2.2 Physico-chemical characteristics of the adsorbent –egg shell

The adsorbent was prepared from dried, crushed and powdered eggshell material of hen and it was sieved in different sizes. Particle size of the adsorbent materials was determined by (i) laser diffraction and (ii) XRD methods. The particle size of the sorbent has been determined for a certain volume packed. The chemical and physical characterization of eggshell and eggshell membrane particles prepared from the hen eggshell waste. Under the characterization measurements investigated, it was found that the pore structures of the two biomaterials belong to a typical Type II, indicating that they should be basically characteristic of nonporous materials or materials with macro pores or open voids. Further, the chemical composition of the resulting eggshell particle was strongly associated with the presence of carbonate minerals from the Fourier transform infrared (FTIR) spectra. In contrast to the resulting eggshell membrane particle, the presence of functional groups of amines and amides was observable because of its chemical composition of fibrous proteins. This powdered material was used as an adsorbent for the removal of chromium in batch mode adsorption and column adsorption studies. The adsorption capacity was determined in both the methods. Column studies were also conducted and better results were obtained.

2.3 Mechanical eggshell traits

To assess eggshell quality in terms of effective thickness (Bain, 1990), parameters, a total of 90 eggs were randomly collected from each breed at 30 weeks of age. The dimensions of eggs (width and length) were measured using a digital caliper to calculate shape index. The thickness (mm) of the shell with intact membranes was measured at three deferent points in the middle part of the egg using a dial gauge micrometer. The shell breaking strength (kg/cm^2) was determined according to Fathi and El-Sahar (Fathi and El-Sahar, 1996). Specific gravity was determined by the flotation method using salt solution with specific gravity ranging from 1.060 to 1.100 at increments of 0.005. Eggshell area was estimated by shell weight per unit of surface area (mg/cm^2), which is an indicator of shell quality and eggs recorded higher significantly higher surface. The egg surface in cm^2 was calculated by dividing shell weight on weight of 1 cm^2 area.

Shell index (g/100 cm^2) was calculated according to following equation (Bain, 2005):

Shell weight (g)/Shell surface (cm^2) x100.

The shell percentage was calculated by (shell weight/egg weight) x100.

2.4 Preparation of samples for ultra structural analysis using SEM

At 30 weeks of age, twenty samples of eggshell were randomly taken from breeds to investigate ultra structural variations. The specimens were prepared by cutting a piece (1 cm^2) of shell from the equatorial region of each egg. The shell membranes were carefully removed by first soaking in water. The loosely adhering membranes were then gently peeled from the edge of the sample inwards. To remove the remaining tightly bound membrane fibers, each sample was then immersed overnight in 6% sodium hypochlorite, 4.12% sodium chloride and 0.15% sodium hydroxide. Thereafter, the specimen was rinsed with water and left to dry at room temperature. Following these preparative treatments, two samples from each egg were mounted in inner side uppermost and in vertically manner on aluminum stubs, coated with gold for 3 min in an Emscope Sputter Coater. These samples were examined using JEOL JSM-T330A scanning electron microscopy at 15 Kv. The incidence of ultra structural variants at the level of the mammillary layer was assessed according to the methodology and terminology developed by the Poultry Research Unit, University of Glasgow (Bain, 1990). The cross-sectional lengths of palisade and mammillary layers were directly measured in µm using scaling software provided with the SEM at a magnification of x200. The total thickness of each gram and brooded in electrical brooding batteries and specimen was measured as the distance from its' rearing cages from 1 day to 14 weeks.

2.5 Adsorption techniques

Broken burette of height about 55 cm and a diameter of about 0.5 cm was chosen for the study. A stopper was provided at the bottom. At the bottom, a plug of cotton was inserted. A known weight of the adsorbent (pulverized egg shells) was added in small quantities with constant tapping. Care was taken to see that the adsorbent was closely packed. A cotton plug was inserted at the top. The height of the adsorbent column was measured. Pure water was admitted through the column. After some time, the stopper was adjusted so as to maintain a constant flow rate. The $K_2Cr_2O_7$ solution of known concentration was added, after draining of water in the tube. The flow rate of the influent was maintained constant. Its concentration was determined by titration against standardized EDTA solution. Adsorption tests were conducted batch wise by taking 25 ml of chromium solution with a known weight of the adsorbent in a highly stopped clean take proof corning bottles in a rotary shaking machines in a constant speed of agitation. The progress of the adsorption process was noted by removing the bottles from the rotary shaking machine at a particular interval of contact times. After removing the bottles from the shaking machine, it was kept in a water bath at room temperature for a time and then filtered. The filtrate was titrated against standardized EDTA solution. The difference between the amount of chromium present initially and that of at the end of a known interval time indicated by the amount of chromium adsorbed by the chosen adsorbent for different concentration of potassium dichromate solution and different weight of adsorbent. The experiments were repeated and the values were noted. Potassium dichromate solution of known concentration (1000 ppm) was prepared. A known volume of the solution (20 ml) was pipetted out into a leak proof bottle, its pH was adjusted from 1-9 by adding hydrochloric acid and sodium hydroxide solution. A known weight (250mg) of the adsorbent, egg shell was weighed accurately and transferred into the bottle. It was then kept shaken in a thermo stated mechanical shaker. After one hour, the bottles were removed from the shaker and filtered. The filtrate was then titrated against standardized hypo solution. The adsorption capacity was determined in both the methods. Column studies were also conducted and better results were obtained.

3. RESULTS AND DISCUSSION

The experimental data reveal the fact that the adsorption of chromium by the eggshell was found to be the maximum of 49% (Table 1). The influence of size of the adsorbent on the chromium adsorption was studied by carrying out the experiment at various sizes 75,150,212 and 300µm. The maximum adsorption was found to be at the size 75µm.

Table 1. Influence of size of adsorbent on percentage adsorption of chromium

Entry	Size of the adsorbent, µm	$[Cr]_{eq}$, ppm (y)	$[Cr]_{ads}$, ppm (x-y)	$[Cr]_{ads}$, % (x-y)/x × 100
01	75	1480.7	1429.4	49.0
02	150	2374.2	535.9	18.0
03	212	2359.2	550.9	18.7
04	300	2297.6	612.5	21.0

[Cr] initial ppm: 2910.1; Weight of adsorbent: 4.0 g; Temperature, °C: 29; Time: 60 min

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. Optimum pH for adsorption studies was found by conducting experiments at various pH (1-9) and maximum adsorption was found to be around 9. Experiments were further carried out at this pH. The influence of pH on adsorption is represented in Figure 1. The effect of the weight of the adsorbent on the adsorption of chromium was studied and the maximum adsorption was found to be at 250 mg /20 ml of chromium (Figure 2). The data revealed the fact that the rate of adsorption increases with increase in the dose of the adsorbent (Anandakrishnanadar et al., 1992). Effect of initial concentration of chromium on adsorption was studied by carrying out the experiment at various initial concentrations around 500,1000,2000,4000 and 10,000 ppm of chromium and weight of the adsorbent being around 250mg/20ml of chromium. The influence of initial concentration of chromium on percentage adsorption is shown in Table 2.

Table 2. Influence of the initial concentration of chromium on percentage adsorption of chromium

Entry	$[Cr]_{initial}$, ppm, (x)	$[Cr]_{final}$, ppm (y)	$[Cr]_{ads}$, ppm (x-y)	$[Cr]_{ads}$, % [x-y /x] ×100
01	1450.0	1123.3	326.7	22.5
02	2797.9	2287.4	510.5	18.2
03	5616.4	4390.9	1225.5	21.8
04	9710.0	7270.7	2430.3	25.0
05	11048.9	8822.8	2226.1	20.1
06	13499.7	10783.4	2716.3	20.1
07	24507.8	20627.4	3880.4	15.8

pH: 2.0; Size of adsorbent: 75µm; Temperature: 29°C; Time: 60 min; Weight of adsorbent: 2.5g

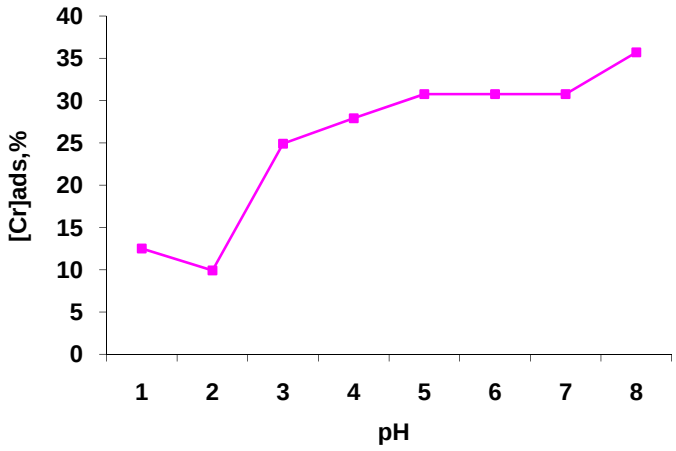

Fig.1. Influence of pH on percentage adsorption of chromium

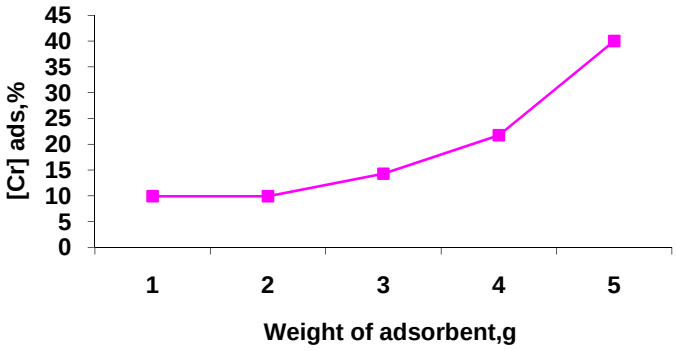

Fig. 2. Influence of the amount of adsorbent of chromium on percentage of adsorption

The effect of time on the percentage of adsorption chromium was studied and shown in Figure 3. It is known that this adsorbent has a capacity to remove the dissolved solute from the solution. Loggergren's equation [log (q_e - q) = logq_e – k_{ad} t /2.303] was applied with a view to understand the nature of adsorption process and the results are presented in Table 3. A linear relation was observed. It indicates the first order nature of adsorption process and also involves the formation of unimolecular layer adsorption (Ananthakrishna Nadar et al., 1992). The k_{ad} calculated on the basis of Loggergren's equation and is found to be 0.008. The value was found to be with the reported value, which again confirms the unimolecularly layer formation, and first order kinetics.

Table 3. Application of Loggergren's Equation to adsorption of chromium

Entry	Time, min	q mg/g	(q_e-q)mg / g	Log (q_e-q)
01	10	264.8	1456.4	3.1633
02	20	264.8	1456.4	3.1633
03	30	529.6	1191.6	3.0761
04	40	794.4	926.8	2.9669
05	50	1191.6	529.6	2.7239
06	60	1721.2	0	0

[Cr] initial ppm: 24507.8; Size of adsorbent: 75µm ; Temperature: 29°C ; Time: 60 min; pH: 2.0; Weight: 2.5 g; qe:1721.2 mg /g

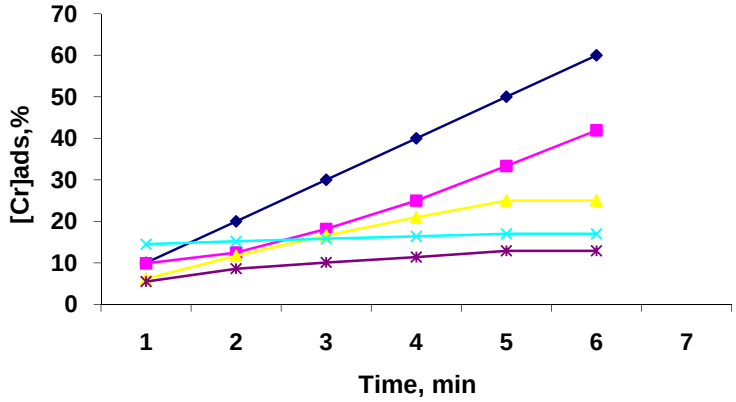

Fig 3. Plot of adsorption of chromium Vs time

Several physico-chemical methods have been widely used for Cr(VI) removal from industrial wastewater, such as ion-exchange, activated charcoal, chemical precipitation, chemical reduction, reverse osmosis, electro dialysis, ultra filtration and adsorption etc. The conventional methods used for the treatment of heavy metals from industrial wastewater present some limitations. There are still some common problems associated with these methods such as incomplete metal removal, high reagent and energy requirement, cost

expensiveness and can themselves produce other waste products that require careful disposal, which in turn have limited their industrial applications.

Removal of chromium by other conventional and popular methods suffer from many disadvantages like the following

(i) High cost/costlier method
(ii) Low efficiency
(iii) No / low recoverability of the adsorbents
(iv) Removing pollutants from one place and causing it to another place

Thus chromium removal using low waste material egg shell may be the best-suited technology in present context to clean up Cr contaminated sites and these technologies are eco-friendly and cost effective.

4. CONCLUSION

The emission of large amount of neutral salt containing a high concentration of chromium tanning waste water will seriously affect the ecological environment. Dealing with scientifically and using waste material effectively to remove chromium present in tanning waste water and solid waste will reduce or even eliminate the negative impact of chromium on environment. A cheap and convenient process for the removal of chromium from its aqueous solution has been developed in this present investigation. This was achieved by the use of new, low cost adsorbent material, eggshell, which is commonly available and economically feasible. The process of removal was found to be enhanced by increasing the dose of the adsorbent. The results were interpreted in the light of Loggergren's equation. Thus chromium removal using low waste material egg shell may be the best-suited technology in present context to clean up Cr contaminated sites and these technologies are eco-friendly and cost effective.

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