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Adsorption Studies Using Chelated Natural Adsorbent For Treatment Of Electroplating Waste Water

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Abstract

Industries using water for various processes generate potential hazard to the environment because of introduction of various contaminations such as heavy metals in to soil and water resources. Heavy metals produced from various industrial process are toxic, non biodegradable and persistent in nature. Chromium is one of major pollutants in the environment and frequently present in wastewaters from various industrial units. The hexavalent form of Chromium is more toxic than trivalent Chromium and is often present in waste water as chromate and dichromate. Hence discharge of heavy metals in aquatic system has become a matter of concern. Many physical and chemical treatments are available for removal. Some of them are expensive, highly energy intensive but also lead to production of harmful by- products. The present study aims at the removal of Chromium (VI) from electroplating industry's wastewater using chelated Delonix Regia. Here chleating agent used is Oxine ie.8- hydroxy quinoline.The characteristics of adsorbent are studied using FTIR, SEM, EDS, XRD analysis. Study of influencing parameters was carried out to evaluate the adsorption capacity of chelated Delonix Regia. This study describes the various methods of investigation and the detailed experimental procedure to obtain the adsorption equilibrium .

Keywords*— Heavy metals, natural adsorbent, Chromium (VI), Delonix Regia ,Oxine*

I. INTRODUCTION

Industrial effluent loaded with various heavy metals is a cause of hazard to human and other forms of life. Among heavy metals Chromium is major pollutant, derived from various industries as effluent. Important industries which generate chromium are paint manufacturing, chrome plating, leather tanning ,textile dyeing, fertilizers, electroplating, cement, mining and photography. Chromium has major impact on environment and it has both beneficial and detrimental properties. Chromium is a metal that exists in several oxidation or valence states, ranging from Chromium (-II) to Chromium (+VI). Chromium compounds are very stable in the trivalent state and occur naturally in this state in ores such as ferrochromate or chromite ore. The hexavalent , Cr(VI) or chromate , is the second most stable state . Hexavalent chromium is more toxic than trivalent chromium. The most common method applied for chromate control is reduction of Cr (VI) to its trivalent form in acid (pH approximately 2.0) and subsequent hydroxide precipitation of Cr (III) by increasing the pH to approximately 9.0-10.0 using lime. Chromium is used in many industrial applications primarily for its anti-corrosive properties and can be generated during welding on stainless steel or metal structures coated chromate paint. .Chromium is used in electroplating (chrome plating). There are some physicochemical methods for Chromium removal i.e. Chemical reduction, Chemical precipitation,Flocculation, Electrolysis, Nanofilteration, Bioaccumulation, Ion exchange, Adsorption on silica composites, Activated carbons, Reverse osmosis, Fly ash, Modified zeolites, Bone charcoal and Microbes. But these methods have some drawbacks, which further create some hazardous effects. So some biological sorption methods are developed to minimise such problems. Adsorption carried by using natural waste by products are called as natural adsorbent derived from plants and can be degraded naturally without causing any harmful effect. Most commonly used natural adsorbents are Orange peelings , Maize bran, Neem saw dust, Mango saw dust, Wheatshell, Sugarcane bagasse, Pineapple crown top etc.. Powders of leaves of some herbal plants like Justicia adhatoda, Cissus

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quadrangulari , Soapnut Acacia have strong affinity towards Chromium (VI) ions from polluted waters·[7]Adsorption remains one of the most economical and widely used method for the removal of toxic pollutants from wastewater and the most widely used Cr (VI) sorbent is activated carbon although it is expensive and has high running costs since it requires regeneration after sorption. Therefore the potential exists for Cr (VI) removal by a lower cost biosorbent.

For the present work ligand loaded Delonix Regia was used as a potential adsosorbent for removal of Chromium in electroplating waste water.

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II .NATURAL ADSORPTION TREATMENT TECHNIQUE

Several authors have studied the adsorption of Cr (VI) from aqueous solution using cellulosic, lignocellulosic and agricultural waste materials.

Agricultural waste and other waste parts of plants like pods, leaves, cover shell, seeds etc are used to remove Chromium from waste water. It is a potential alternative to conventional methods to eliminate toxic effect of heavy metals like Chromium , Lead, Arsenic, mercury etc. The major advantages of this technique over the conventional methods are

- Low cost,
- Easily available,
- Create less hazardous effects
- Low energy intensive
- Lead to production of harmless by-products
- Reducing secondary pollution

Agricultural waste as natural adsorbents have good adsorption properties. Delonix Regia was also used for removal of Chromium.[8] For present study chelated Delonix Regia is used as adsorbent for natural adsorption technique.

III .OBJECTIVES

1. Characterization studies of adsorbent and waste water.
2. To validate percentage removal efficiency to different adsorption models.

IV. MATERIALS AND METHODS

IV.A. Chemicals :

All chemicals used were of analytical grade and solutions were made with distilled water. Chemicals required are Potassium Dichromate , 1 N Sulphuric acid , 50% NaOH, 1 N Nitric acid, Oxine. Water used in all experiments was obtained from distillation unit in our laboratory.

IV.B. Preparation of Stock solution :

Stock solution of 100 ppm was prepared by dissolving suitable amount of A. R. Potassium Dichromate in distilled water. Calibration curve was determined using Atomic Absorption Spectrophotometer.

IV.C. Preparation of Adsorbent :

The pods were cut into small pieces , dried in sunlight for 5 days and further dried in a hot air oven at 60 degree centigrade for 24hrs.The completely dried material was powdered well , chemically activated by treating with concentrated sulphuric acid with constant stirring and kept for 24 hrs. times The carbonized material obtained washed well with water several times to remove excess acid and pH balanced Then remaining mass was dried at 105-110 degree centigrade in a hot oven for 24 hours. Then the adsorbent was obtained was ground well and sieved through 425 micron mesh and kept in a air tight container for further use.

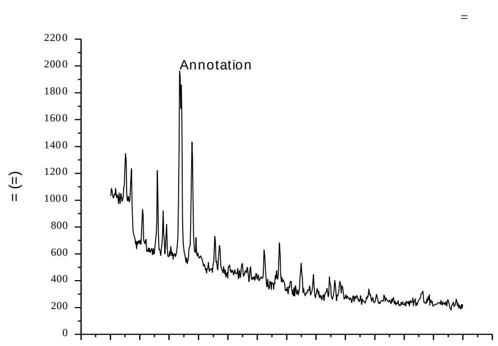
IV.D. Chelation of Adsorbent:

100 ml of $1x10^{-4}$M Oxine solution is prepared . In that solution required amount of adsorbent is mixed and stirred by magnetic stirrer for 8 hours. Then filtered and dried to normal temperature . This chelated Delonix Regia is used for experimental work as adsorbent.

V CHARACTERIZATION OF ADSORBENT

V. 1.XRD Analysis

Before adsorption low intensity peaks were observed which confirms the amorphous nature of Delonix Regia . But strong intensity peaks were observed between 22.5 to 35 (2 theta) in X-ray diffractogram for Delonix Regia seeds as shown in graph. It indicates the some amount of crystalline nature of Delonix Regia .



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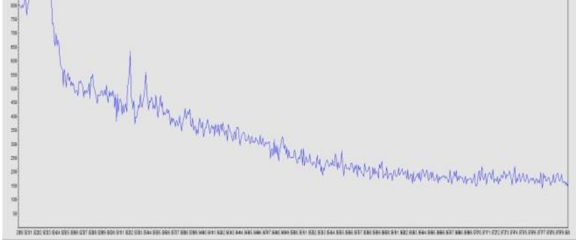

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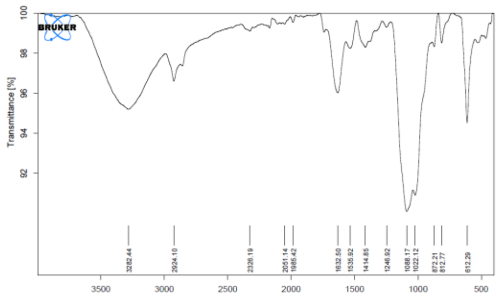
Fig. 1. XRD Of Powder of Delonix Regia Seeds(Before test)   Fig. No. 2. XRD Of Powder of Delonix Regia Seeds(After test)

After peaks observed between 22.5 to 35 (2 theta) in X-ray in XRD of before adsorption are not observed in XRD image after adsorption in which amorphous nature is clearly indicated.

V.2. FTIR Analysis

The FT –IR spectra of the adsorbents were measured within the range of 400-4000cm^{-1} wave number. The FT-IR spectra of the adsorbent display a number of adsorption peaks indicating the complex nature of the studied adsorbents . Before adsorption peak at 3282.44cm-^{1} is characteristic of O-H bond stretching . Peaks at 2924 .10 cm-^{1} is due to stretching of N-H bond, Peaks at 1414.85 cm-^{1} is due to O-H bending.Peaks at 872.21 cm-^{1} is due to C-H bonding.Peaks at 612.29 cm-^{1} is due to C-X bonding .



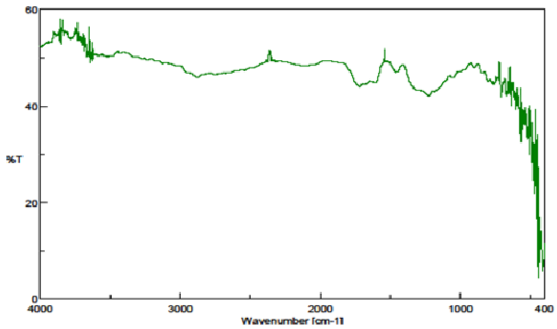
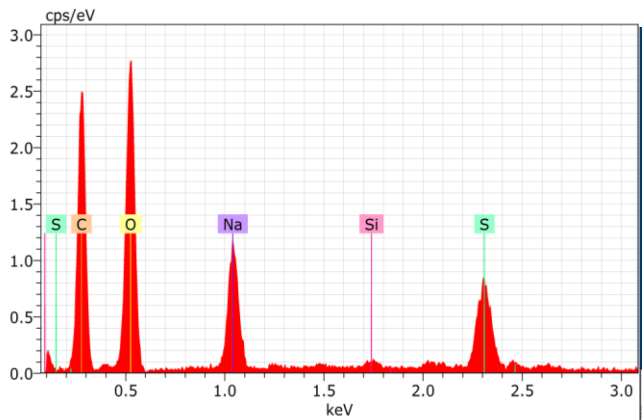
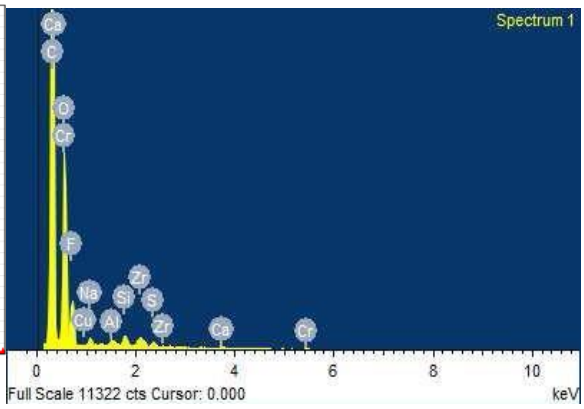


Fig. 3. FTIR Of Powder of Delonix Regia Seed (Before test)   Fig. No.4 FTIR Of Powder of Delonix Regia Seeds(After test)

After adsorption broad peaks observed at 3282.44cm^{-1} are replaced by narrow peak which indicate breakage of O-H bond. So alcohols or phenols group is replaced. Region between 2000-1650 cm^{-1}shows overtone region. Narrow peak at 1535.92 shows bending of -CO-N-H bond. Broad peaks observed at 1414.85cm^{-1} are replaced by narrow peak which indicate breakage of O-H bond. Small peak at 1246.92 cm^{-1} shows ether i.e. aromatic group is present in small amount. Small peak at 1022.12cm^{-1} shows aliphatic amines group present is in small amount. So some functional groups present in Delonix Regia are removed, which is indicated that adsorption takes place .

V. 3. EDS Analysis





. No. 5 EDS Analysis Of Powder of Delonix Regia Seeds (Before Test) Fig. No. 6 EDS Of Powder of Delonix Regia Seeds(After test)

Before adsorption oxygen, carbon , Sodium , sulphur and silicon elements were present. All elements present are in K series. Chromium is absent in given spectrum. From above graph it was observed that after adsorption in spectrum additional iron , aluminum, calcium , chromium , copper , zinc elements are observed. These are heavy metals which

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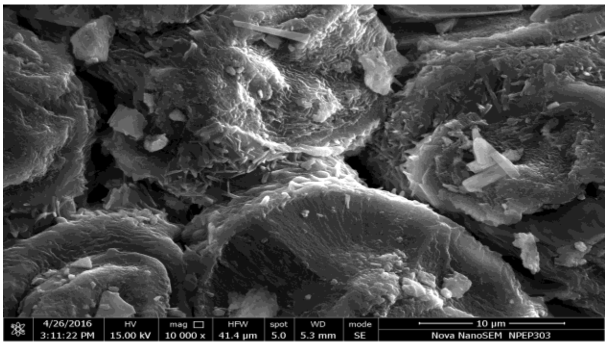
are removed after adsorption which indicates that adsorption takes place.

V.4 FESEM Analysis

In below photo internal microscopic structure of Delonix Regia adsorbent is observed using Field emission scanning electron microscopy (FESEM), The corresponding SEM Micrographs being obtained using at an accelerating voltage of 15kV and magnification of X 10000.Before adsorption Delonix Regia showed rough areas of surface on which micro pores and macro pores were clearly identifiable Surface texture analysis was carried out using a Scanning Electron Microscope (SEM). SEM images show the porous surfaces texture of adsorbent . Micro pores and macro pores which were seen before adsorption were

filled by Chromium. Total surface is filled by Chromium ions. So appearance of porous structure become cloudy. Cloudy appearance shows that adsorption takes place.



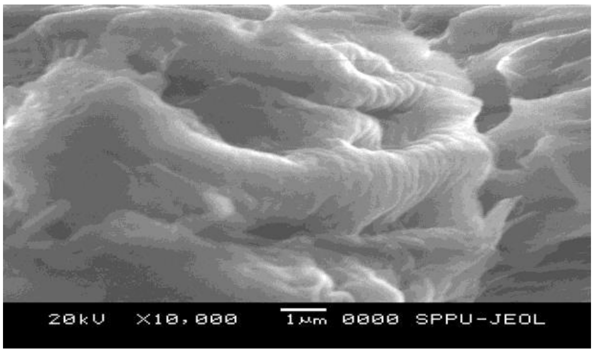


Fig. no.7 FESEM Analysis With 10000X Magnification Fig. No. 8 SEM Of Powder of Delonix Regia Seeds(After test)

VI. RESULTS AND DISCUSSION

The analysis of various chemical properties has been done to understand the composition of electroplating industry effluent. The effluent samples were collected from the Electroplating industry MIDC, Dhayri Pune, Maharashtra, India. The sample bottles were filled, labeled and transported to the laboratory, stored and chemical analysis of the samples were analyzed in department of Civil Engineering, Environmental Research Laboratory of Sinhgad College of Engineering at Pune.

Sr. No.	Parameters	Unit	Value
1	pH	-	**2.79**
2	Chemical Oxygen Demand	mg/l	3760
3	Biochemical Oxygen demand	mg/l	815
4	Total Solids	mg/l	2384
5	Total Dissolved Solids	mg/l	2384
6	Total Suspended Solids	mg/l	00
7	Total Heavy metals	mg/l	1290
8	Total Chromium	mg/l	**764**
9	Hexavalent Chromium	mg/l	**761.9**
10	Trivalent Chromium	mg/l	2.1

Table No. 1 Characteristics of raw water

So given water sample is acidic in nature , having maximum COD, no suspended solids, contain Chromium as heavy metal in more quantity. Chromium available in water is in hexavalent state.

VI.B. Adsorption Isotherm Study

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Adsorption isotherm is the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. The quantity of adsorbate (waste water sample) that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperatureFor isotherm study adsorbent dose varied from 0.2 gm to 5 gm. For each dose 100 ppm stock solution of 100 ml quantity is taken and solution is shaken for 8 hours by magnetic stirrer.

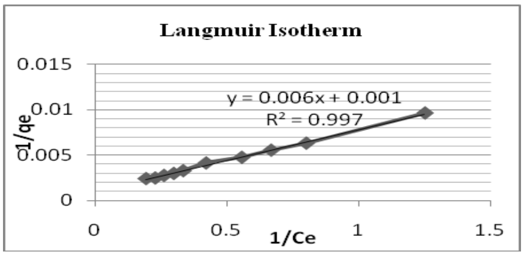


Fig. No. 9 Langmuir Isotherm

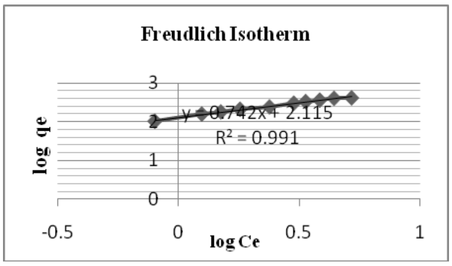


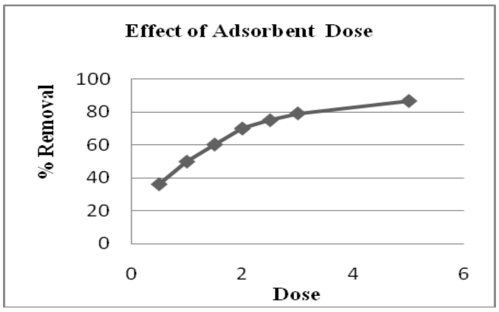
Fig. No. 10 Freundlichisotherm

According to Langmuir isotherm the R^2=0.997, Freundlich isotherm the R^2=0.991which are equal to unity. This shows that Langmuir isotherm is best fitted for adsorption phenomenon

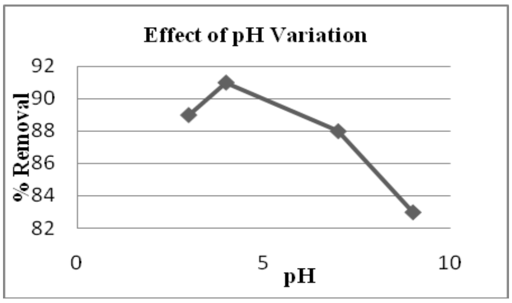
VI.C. Equilibrium Study

Equilibrium study was carried out in batch process to study various parameters like effect of adsorbent dosage, effect of contact time, effect of pH, effect of speed agitation and effect of temperature were studied to obtained equilibrium point.

VI.C.1 Effect of adsorbent dose :

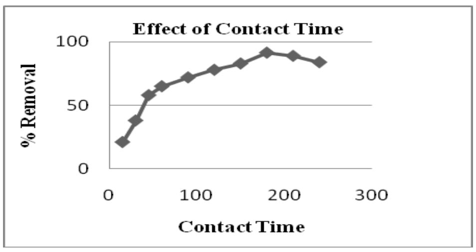


VI.C.2 Effect of pH Variation

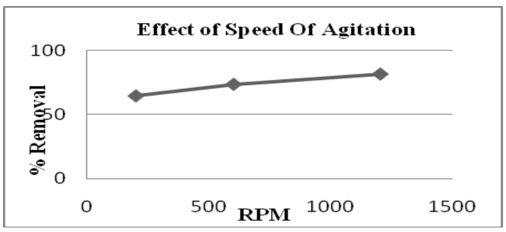


Maximum Chromium removal is at 5 gm of adsorbent dose and at pH 4.

VI.C.3. Study of Effect of Contact Time

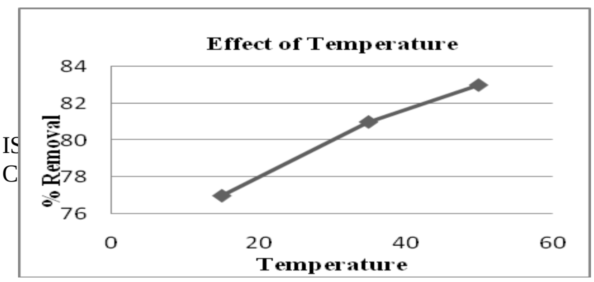


VI.C.4. Study of Effect of Speed of Agitation



Maximum contact time is 180 minutes for Chromium removal at 1200 rpm speed

VI.C.5. Study of Effect of Temperature



The maximum % removal efficiency was found to be 1200 rpm at 50^0C.

VI. D. Column Study

Column study was carried out by considering parameters like bed height, column diameters and flow rates. Hexavalent chromium sample was passed through the ligand loaded (chelated) Delonix Regia which adsorbed and remove Cr (VI).

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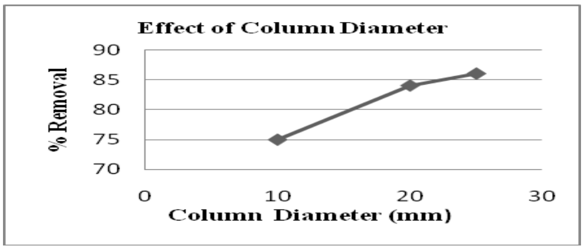
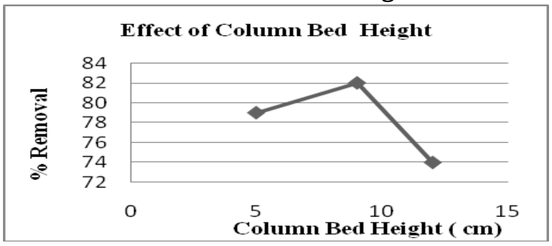
VI.D.1 Effect of column Diameter

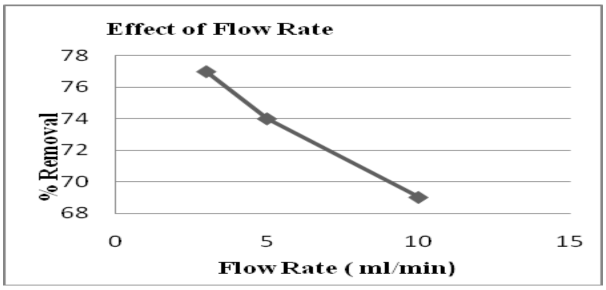


VI.D.2 Effect of Column Bed Height



Optimum Removal was found at 25 mm diameter, 9cm bed height and at 3ml/min flow rate .

VI.D.3 Effect of flow rate



VII . CONCLUSION:-

The following conclusions can be drawn from this study.The operational parameters such as adsorbent dose, contact time, pH, speed of agitation and temperature were found to have an effect on the adsorption efficiency of ligand loaded Delonix Regia .The experimental data on batch study showed the maximum removal of 86.66 % was obtained, 0.5 gm of adsorbent and 100ml of Cr (VI) sample with decreasing initial concentration and increasing contact time of adsorbent. The runs were carried out for 6 hrs for equilibrium.Values of correlation coefficient for Langmuir isotherms is 0.997where as for Frendlich the values is 0.991. It clearly indicates that Langmuir isotherms fit well for adsorption equilibrium.The removal of Cr (VI) from solution strongly depends pH of the solution , adsorbent dosage , initial Cr (VI) concentration and contact time. The maximum adsorption of Cr (VI) was obtained at pH 4.0, adsorbent dosage of 5 gm, contact time 180 min, temperature at 50^0C and1200 rpm speed of agitation. From Column study it can be said that maximum adsorption of Cr (VI) was obtained at flow of rate of 3ml/min, bed height 9 cm and column diameter 25 mm. With increase in flow rate adsorption decreases and with increase in column diameter, the adsorption also increases.

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REFERENCES

[1] Smita Samdani , S.J. Attar, Chetan Kadam , Saroj S. Baral: Treatment of Cr(VI) contaminated waste water using Biosorbent , Hydrilla Vericillata, International J. Of Engg. Research & Indu. Appls(IJERIA); 271-282,2008
[2] S.H. Hasan, K.K. Singh, O. Prakash , M.Talat, Y. S.Ho: Removal of Cr(VI)from aqueous solutions using agricultural waste ‘maize bran’, Journal of Hazardous materials , 52, 356-365, 2008
[3] V. Vinodhini , Nilanjana Das : Biowaste materials as sorbents to remove chromium (VI) from aqueous environment – A comparative study, ARPN Journal of Agricultural and Biological Science , Vol.4, No. 6, 19- 23,2009
[4] V. Vinodhini, V.Anabarasu , Nilanjana Das: Screening of natural waste products for Cr(VI) ions from industrial effluents ,Indian journal of natural Products and Resources , Vol.1(2), 174-180, June 2010,
[5] Mohammad Reza Hadjmohammadi, Mina Salary And Pourya Biparva,Removal Of Cr (Vi) From Aqueous Solution Using Pine Needles Powder As A Biosorbent , journal of applied sciences in Environmental Sanitation ,vol.6, 1-13. 2011
[6] M. Sen, M. Ghosh Dastidar: ReviewChromium Removal Using Various Biosorbents ,Iran. J. Environ.

ISSN: 2233-7857 IJFGCN

Health. Sci. Eng, Vol. sor7, No. 3, pp. 182-190,2010

[7] K. P.C. Sekhar, R. V. Vishnu Babu, D. Srividhya, K. Ravindhranath : Removal of Chromium (VI) from Waste Waters Using Leaves Powders ofJusticia adhatoda, Cissus quadrangularis, Soapnut Acacia, Scholars Research Library, Der Pharma Chemica, 4 (2):664-673 ,2012.

[8] R.H. Krishna Reddy, N. Naga Malleswara Rao, J. V. Suman Krishna , K. Ravindhranath :Removal Of Chromium
(VI) From Polluted Waters: A Biological Approach ,Journal Of Pharmaceutical And Biomedical Sciences, 17 (04), 1-6, 2012

[9] G.V. Subha Rao, S. Durga Rao, R. Srinivasa Rao, M. Appaiah , K. Ravindranath : Removal of Chromium (VI) From Polluted Water Using Biosorbents Derived From Some Herbal Plants, Journal of Indian Water Works Association , Vol.4, 307-3014, 2012,

[10] Farai Mutongo, Olga Kuipa and Pardon K. Kuipa :Removal of Cr (VI) from Aqueous Solutions using Powder of Potato Peelings as a Low Cost Sorbent,

[11] Shadreck Mandina, Fidelis Chigondo, Munyaradzi Shumba, Benias Chomunorwa Nyamunda, Edith Sebata
:Removal of er chromium (VI) from aqueous solution using chemically modified orange (citrus cinensis) peel, IOSR Journal of Applied Chemistry (IOSR-JAC) , Volume 6, Issue 2 ,PP 66-75,(Nov. – Dec. 2013)

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