Biosorption Efficiencies of *Mangifera indica, Ficus racemosa* and *Syzygium cumini* barks for Chromium (VI) Removal from Tannery Polluted waters of Unnao Industrial Area, Uttar Pradesh

Supriya Singh*, Alka Tripathi*& S K Srivastava**

*Department of Applied Sciences, Institute of Engineering & Technology,
Sitapur Road Yojana, Lucknow - 226021 (India). Email; supriyalu@gmail.com
**Central Ground Water Board, Govt of India, Bhujal Bhawan,
Sitapur Road Yojana, Lucknow - 226021 (India). Email; sudhir63@yahoo.co.in

Abstract- The presence of chromium (VI) in ground water of Unnao Industrial area, Uttar Pradesh, India has been found up to 5.36 mg/l and due to its health impact on human body it is essential to search for new remedial measures for its removal from drinking water sources. The area contains a number of tanneries and the resulted solid / liquid waste is dumped in the nearby areas. Chromates are often used to manufacture, among other things, leather products, causes allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers. The acute toxicity of chromium (VI) is due to its strong oxidative properties. After it reaches the bloodstream, it damages blood cells by oxidation reactions. Hemolysis, and subsequently kidney and liver failure, are the results of this damage.

Due to severe health impact of Cr (VI) on human body the removal becomes more essential particularly from the drinking water. Conventional methods for removal include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction .These methods for removal of heavy metals from wastewaters however, are often not economically appealing because of high operational cost. The search for new technologies involving the removal of chromium from tannery wastewaters of Unnao industrial area has directed attention to biosorption, based on metal binding capacities of various biological materials. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal, minimization of chemical / biological sludge and ecofriendly. The objective of this study is to develop inexpensive and effective biosorbent that is easily available in large quantities and feasible economically for Cr (VI) metal ions in solution.

Here, biosorbent has been prepared from easily available *Mangifera indica / Ficus racemosa / Syzygium cumini* bark to carry out chromium (VI) removal from tannery contaminated water. The parameters investigated are contact time, adsorbent dosage, temperature, variable initial chromium (VI) concentration and pH. The adsorption process of chromium (VI) is tested with Linear, Langmuir and Freundlich isotherm models. The results of *Mangifera indica* bark on the Langmuir isotherm to the systems yielded maximum adsorption capacity of 19.64 mg/g at 30 ^{o}C at a solution pH of 7. The adsorption was found maximum up to 80.2% at low pH in the range of 1-3.The contact time of 60 min resulted to the 67% adsorption of metal in 5mg/L solution using adsorbent dose of 1g/L. While the *Ficus racemosa* bark on application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 25.9 mg/g at 30°C at a solution pH of 7. The adsorption of chromium (VI) was found to be maximum up to 83.78% at pH in the range of 1-3.The contact time of 60 min resulted to the 36.82% adsorption of metal in 50mg/L solution using adsorbent dose of 1g/L . *Syzygium cumini* bark on application of the Langmuir isotherm to the systems yielded maximum adsorption capacity of 31.51 mg/g at a solution pH of 7 having Cr (VI) concentration 50 mg/L and biosorbent dose 1g/L. The adsorption of chromium (VI) was found to be maximum 95.63% at low pH values of 2 having Cr (VI) concentration 50 mg/L and biosorbent dose 1g/L. The contact time of 60 min resulted to the 55.28% adsorption of metal in 50mg/L solution using adsorbent dose of 1g/L.

The hexavalent chromium removal efficiency of *Syzygium cumini* bark has been found better as compared to *Mangifera indica & Ficus racemosa* barks and it can used for removal of chromium (VI) from the tannery polluted water as a low cost biosorbent. The FTIR technique was also carried out to correlate the adsorption sites of biosorbent.

Keywords: Comparative Biosorption efficiency; Chromium (VI); *Mangifera indica, Ficus racemosa* and *Syzygium cumini* barks; Linear, Freundlich & Langmuir isotherm.

INTRODUCTION

The carcinogenity of chromate dust has been known for a long time, and publications describe the elevated cancer risk of workers in a chromate dye company. Chromium salts (chromates) are also the cause of allergic reactions in some people. Chromates are often used to manufacture, among other things, leather products, paints, cement, mortar, and anti-corrosives. Contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers. The LD_{50} for chromium (VI) ranges between 50 and 150 mg/kg. (Katz

etal 1992). In the body, chromium(VI) is reduced by several mechanisms to chromium(III) already in the blood before it enters the cells. The chromium(III) is excreted from the body, whereas the chromate ion is transferred into the cell by a transport mechanism. The acute toxicity of chromium(VI) is due to its strong oxidative properties. After it reaches the bloodstream, it damages blood cells by oxidation reactions. Hemolysis, and subsequently kidney and liver failure, are the results of this damage. (Basketter, etal 2000).

Hexavalent chromium in the surface and ground water is hazardous to the environment because of its high toxicity, high potentiality to contaminate drinking water sources (BIS 1991), possible human health risk and finally to its pollution on ecosystem. In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement. Among the different heavy metals, chromium is a common and very toxic pollutant introduced into natural waters from a variety of industrial wastewaters (Srivastava et al.2013). The two major sources of contamination are tanneries (trivalent chromium), electroplating and metal finishing industries (hexavalent chromium). Chromium occurs most frequently as Cr (VI) or Cr (III) in aqueous solutions (Dakiky et al. 2002). Both valency of chromium are potentially harmful but hexavalent chromium possesses a greater risk due to its water soluble nature and high penetrating power to enter into the living cells (Dakiky et al. 2002), which leads to its carcinogenic properties. Hexavalent chromium, which is primarily present in the form of chromate CrO_4^{--} and dichromate $Cr_2O_7^{--}$, has significantly higher levels of toxicity than the other valence states (Sharma & Forster 1995).

In general, chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, and evaporation, etc. (Singh et al. 2014). However, these methods are cost intensive and are unaffordable for large scale treatment of wastewater which is rich in chromium (VI). Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular (Jianlong et al. 2000, Sharma & Bhattacharyya 2004). Other commercial adsorbents are recently reported to have been used in industries, although their versatility and adsorption capacity are generally less than those of activated carbon (Gupta & Babu 2006).

Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction (Tripathi et al. 2013), reduction followed by chemical precipitation (Ozer et al. 1997), adsorption on the activated carbon (Lotfi M. & Adhoum 2002), solvent extraction (Mauri et al.2001), freeze separation, reverse osmosis (Padilla & Tavani 1999), ion-exchange (Rengaraj et al. 2003) and electrolytic methods (Namasivayam & Yamuna 1995). These methods have found limited application because they often involve high capital and operational costs. Biosorption is an effective and versatile method for removing chromium. Natural materials which are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed off without expensive regeneration. Most of the low cost biosorbent have the limitation of low sorptive capacity and thereby for the same degree of treatment, it generates more solid waste (pollutant laden sorbent after treatment), which possess disposal problems. Therefore, there is need to explore low cost biosorbent having high contaminant sorption capacity. Use of locally available adsorbents has been suggested by Nourbakhsh et al. (1994) and Bai and Abraham (2003) and agricultural byproducts (Bailey et al. 1999) for heavy metal removal. However, the literature is still insufficient to cover this problem and more work and investigations are needed to deal with other locally available and cheap biosorbent to eliminate Cr (VI) discharged by industrial wastage (Singh et al 2013 and 2014). The present paper deals with the comparative efficiencies of *Mangifera indica, Ficus racemosa* and *Syzygium cumini* barks for Chromium (VI) removal from tannery effluent waters.

Mangifera indica, Ficus racemosa and *Syzygium cumini* is a very common tree in tropical countries. It is grown mainly for its fruits and wood. The phytochemical investigated in the *Mangifera indica* bark extract are mostly phenolic constituents: gallic acid, 3,4-dihydroxy benzoic acid, gallic acid methyl ester, gallic acid propyl ester, mangiferin,(+)-catechin, (-)-epicatechin, and benzoic acid and benzoic acid propyl ester (Tanaka et al. 1984). The astringent nature of the *Ficus racemosa* bark has been employed as a mouth washes in spongy gum and also internally in dysentery, menorrhagia and haemoptysis (Tanaka et al. 1984). Phytochemical constituents isolated from S. cumini (L.) stem bark has been found to contain betulinic acid, friedelin, epi-friedelanol, β-sitosterol, eugenin and fatty acid ester of epi-friedelanol (Sengupta and Das, 1965), β-sitosterol, quercetin kaempferol, myricetin, gallic acid and ellagic acid (Bhargava *et al*, 1974), bergenins (Kopanski and Schnelle, 1988), flavonoids and tannins (Bhatia and Bajaj, 1975). The presence of gallo- and ellagi-tannins may be responsible for the astringent property of stem bark. Literature survey reveals that in most of the peer reviewed journals the comparative adsorption efficiency of Cr (VI) with *Mangifera indica, Ficus racemosa & Syzygium cumini* bark as biosorbent yet has not been investigated, and this is the first such study undertaken by the authors. The effect of pH, contact time, temperature, initial hexavalent chromium concentration, variable adsorbent doses and adsorption equilibria were investigated. FTIR of adsorbent and chromium adsorbed adsorbent was also carried out for spectral studies.

METHODS & MATERIAL

The Chromium (VI) contaminated waters were collected from Unnao industrial areas of Uttar Pradesh for experimental biosorption removal. The estimation of hexavalent chromium in the solution at different conditions and time interval was carried out by using Diphenyl carbazide method as per standard methods (*APHA* 1995). Shimadzu UV-VIS Spectrophotometer at 540 nm was used for measurement. All the chemicals used were of analytical reagent grade. The standard stock Cr(VI) solutions was prepared by weighing 2.8287 g of Potassium dichromate in one liter double distilled water and it was further diluted to desired concentrations

containing 1,2,4,5,6,8,10,20, 40, 50, 60, 80, 100, and 200 mg/L of chromium (VI)in aqueous phase standard solutions. The Cr (VI) loadings on sorbents were computed based on mass balance through loss of metal from aqueous solution. The pH of solution was maintained using 0.5 N HCl and 0.5 N NaOH solutions. The temperature of the solutions was maintained by using temp. regulatory oven. The FTIR of the sorbent (*Mangifera indica, Ficus racemosa & Syzygium cumini* bark) and chromium loaded was carried out using Bruker FTIR Spectrophotometer for absorption peaks.

Preparation of Biosorbent (Mangifera indica, Ficus racemosa & Syzygium cumini bark powder)

The sorbents used was powder of *Mangifera indica, Ficus racemosa & Syzygium cumini* barks. The material was obtained from local area. There after it was washed, dried and then pulverized in pulverizer and air-dried in the sun for five days. After drying, the bark powder was kept in air tight plastic bottles. The powdered material was used as such and no pretreatment was given to the materials. The particle size was maintained in the range of 212–300 μm (geometric mean size: 252.2 μm).

Screening of Biosorbent

The experiments were carried out in 150 mL borosil conical flasks by agitating a pre-weighed amount of powdered adsorbent of *Mangifera indica, Ficus racemosa & Syzygium cumini* bark with 10 - 100 mL of the aqueous chromium (VI) solutions for a predetermined period at 10-40°C in an ice bath / oven. The biosorbent doses were maintained 1-5 g/L for different experiments. The adsorbent is filtered with whatman filter paper no 41 from aqueous solution for analysis of hexavalent chromium on spectrophotometer. Adsorption isotherm study is carried out with different initial concentrations of chromium (VI) from 20 to 100 mg/L with the adsorbent dosage of 1-5 g/L. The effect of pH on Cr (VI) biosorption was studied at 30^{0}C with chromium (VI) concentration of 50 mg/L and an adsorbent dosage of 4 g/L. The effect of adsorbent dosage is studied by varying the adsorbent amount from 1 g/L to 5 g/L with chromium (VI) concentration of 50 mg/L. The effect of temperature varying from 10- 40°C was studied at Cr (VI) concentration of 50 mg/L and biosorbent dose of 4 g/L. The time duration 60-300 min was studied on Cr (VI) concentration of 5 mg/L and biosorbent dose of 4 g/L.

The equilibrium concentration of free chromium (VI) ions at different experimental conditions with suitable time interval in the solution was determined by filtering the adsorbent loaded with hexavalent chromium through whatman filter paper followed by developing a purple-violet color in the filtrate with 1, 5-diphenyl carbazide in acidic medium as complexing agent spectrophotometrically. The absorbance of the purple-violet colored solution was read at 540 nm after 20 min.

RESULTS AND DISCUSSION

Mangifera indica, Ficus racemosa & Syzygium cumini bark has been used for chromium (VI) removal from aqueous solutions in the present study. Figure -1 shows the adsorbent capacity of various adsorbents. The comparatively study with other non-conventional adsorbents reveals that present study of adsorbent prepared from *Syzygium cumini* bark has better adsorption capacity in many cases (biomass residual slurry, Fe (III)/Cr (III) hydroxide, waste tea, walnut (shell); comparable adsorption capacity with palm pressed-fibers, maize cob, sugar cane bagasse and lower adsorption capacity with activated carbon & saw dust for chromium (VI) ions (Huang &Wu 1977, Namasivayam & Ranganathan 1993,Orhan & Buyukgungur 1993, Tan et al. 1993,Sharma & Forster 1994, Namasivayam & Yamuna1995, Gupta & Babu 2008).
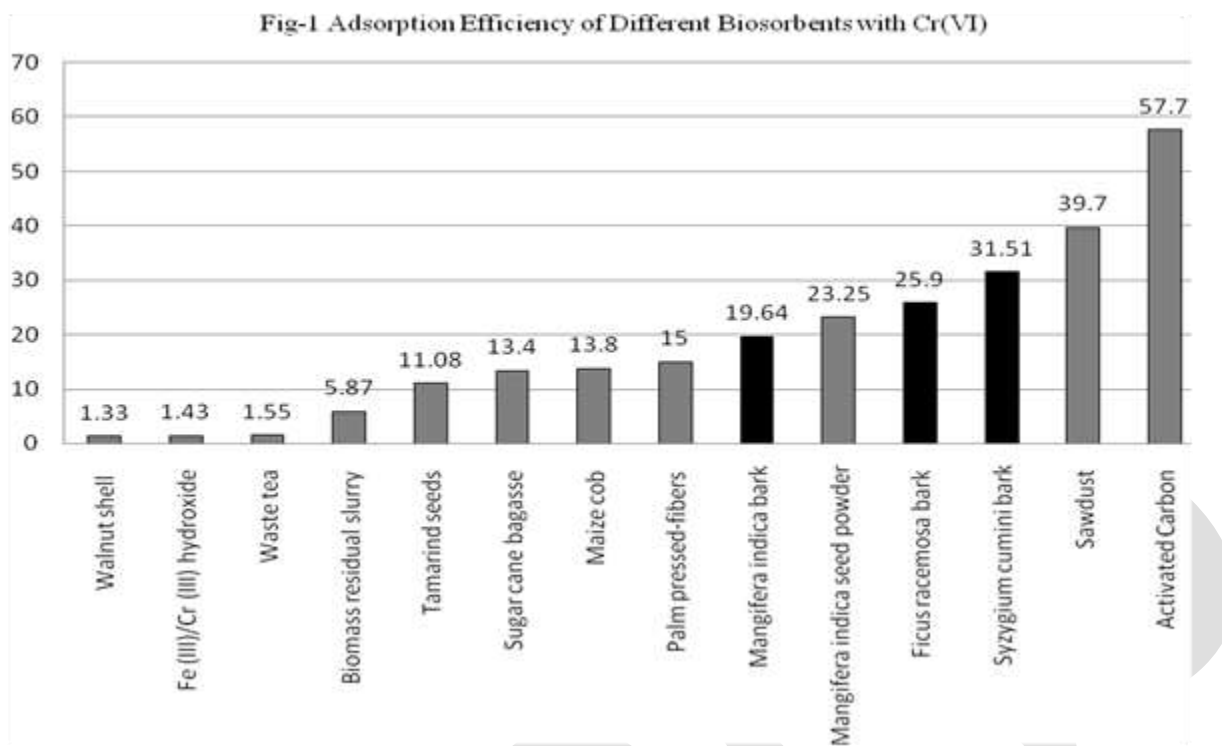
Fig-1 Biosorption capacity of various adsorbents for Hexavalent Chromium

Effect of Contact Time on Chromium (VI) Adsorption

The effect of contact time up to 300 min. on chromium VI adsorption was studied using biosorbent dose of 1 g/L and hexavalent Chromium concentration of 4, 5 & 50 mg/L.(Fig -2). The extraction process was carried out with standard Cr (VI) 100 mL solution of 4 5 and 50 mg/L in 150 mL conical flask with biosorbent dose of 1g/L and the concentration of hexavalent chromium in the solution was recorded by filtration through whatman filter paper followed by development of colour using Diphenyl carbazide at 540 nm in time interval of 60, 120, 180, 240 and 300 minutes. Most of the adsorption takes place in first hour of contact and longer contact time has negligible effect on extraction of chromium (fig-2). In present experimental conditions low concentration solution of Cr (VI) is more rapidly removed by *Mangifera indica* bark (80% approx).
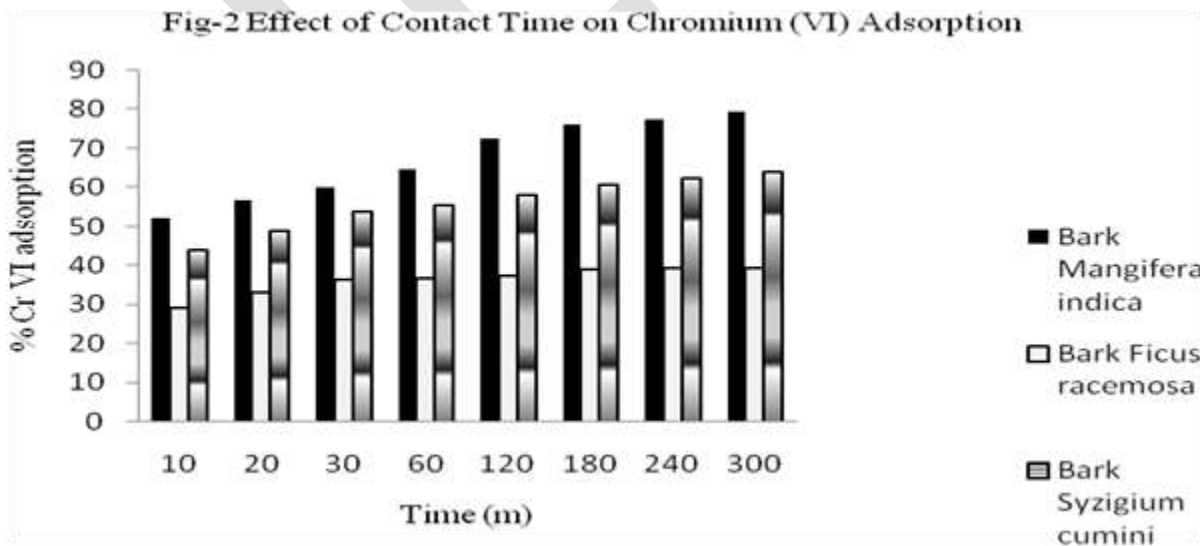

Fig-2 Effect of Contact Time on Chromium (VI) on *Mangifera indica, Ficus racemosa & Syzygium cumini* bark biosorption

Effect of Increasing Concentration of Cr (VI) on Adsorption

Standard Cr (VI) solutions of 100 mL having initial concentration of 1, 2, 4, 6, 8 and 10 mg/L were treated with biosorbent 0.1 g dose in each solution. The concentration of Cr (VI) in the solution was determined using the standard methods. The percentage adsorption increases up to 85.9 for 4 mg/L Cr (VI) concentration in *Mangifera indica* bark there after it decreases (figure-4) where as in *Ficus racemo*sa bark the adsorption increases up to 82.9 for 4 mg/L Cr (VI) concentration there after it decreases (figure-3). The percentage adsorption slowly decreases from 67.6 for 10 mg/L to 50.88 for 10 to 50 mg/L Cr (VI) concentration solutions for *Syzygium cumini* bark.
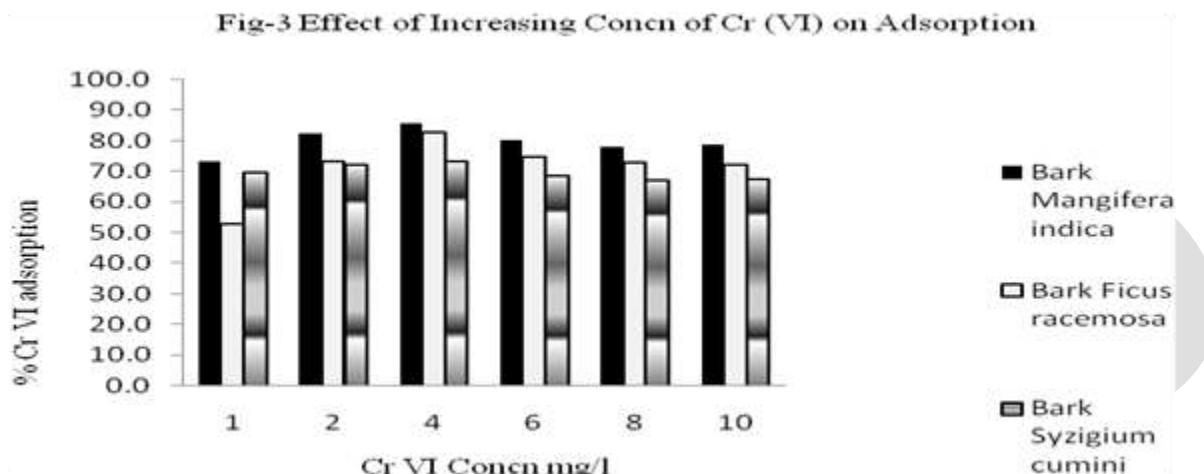
Fig-3 Effect of Increasing Concn of Cr (VI) on *Mangifera indica, Ficus racemosa & Syzygium cumini* bark biosorption

Effect of Temperature on Cr (VI) biosorption

The 100 mL samples of 50 mg/L hexavalent chromium concentration in 150 mL conical flasks were treated with 0.1 g of biosorbent (*Mangifera indica, Ficus racemosa & Syzygium cumini* bark powder) maintained at 10, 20, 30 & 40 °C. The solutions were kept for 60 min. with gentle shaking at periodical intervals and the concentration of Cr (VI) was measured in the solution after filtering through Whatman filter paper by developing the colour using Diphenyl carbazide at 540 nm spectrophotometrically. The percentage biosorption of Cr (VI) was found maximum at 40 °C and minimum at 10 °C showing an increasing trend with temperature. (Figure-4)
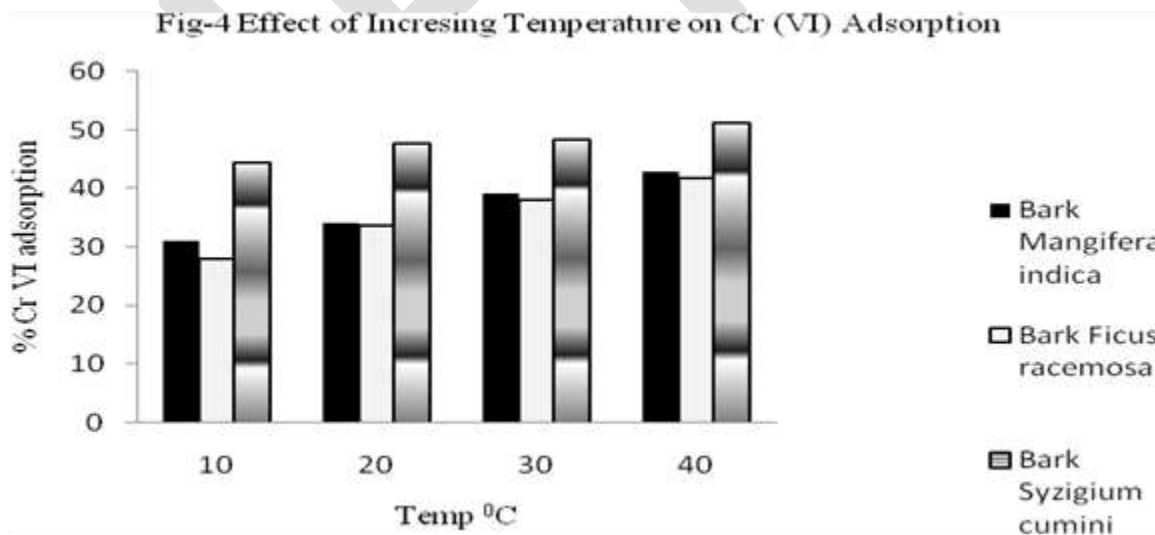

Fig-4 Effect of Temperature on Cr (VI) biosorption using *Mangifera indica Ficus racemosa & Syzygium cumini* bark

Effect of pH on Cr (VI) biosorption

The experiments using 100 mL of 50 mg/L Cr (VI) solutions for 60 min time and adsorbent dose of 0.1 g were carried out at pH 2, 4, 7, 10 and 12 and the biosorption of Cr (VI) is depicted in figure-5. The *Mangifera indica* bark in acidic medium (pH-2) has

been found to show maximum biosorption up to 80% of initial chromium (VI) which decreases to 13% at neutral (pH-7) and further increases to 26% in basic medium (pH-12).(Figure-5). *Syzygium cumini* barks in acidic medium (pH-2) has been found to show maximum biosorption up to 95.63% of initial chromium (VI) which decreases to 63.02% at neutral (pH-7) and further decreases to 52.98% in basic medium at pH-12 *& Ficus racemosa* is also comparable to it showing maximum biosorption up to 83.78% of initial chromium (VI) which decreases to 51.8% at neutral (pH-7) and further increases to 58.1% in basic medium (pH-12)The *Syzygium cumini* bark has been found to better in biosorption efficiency due to its more percentage adsorption near neutral medium.
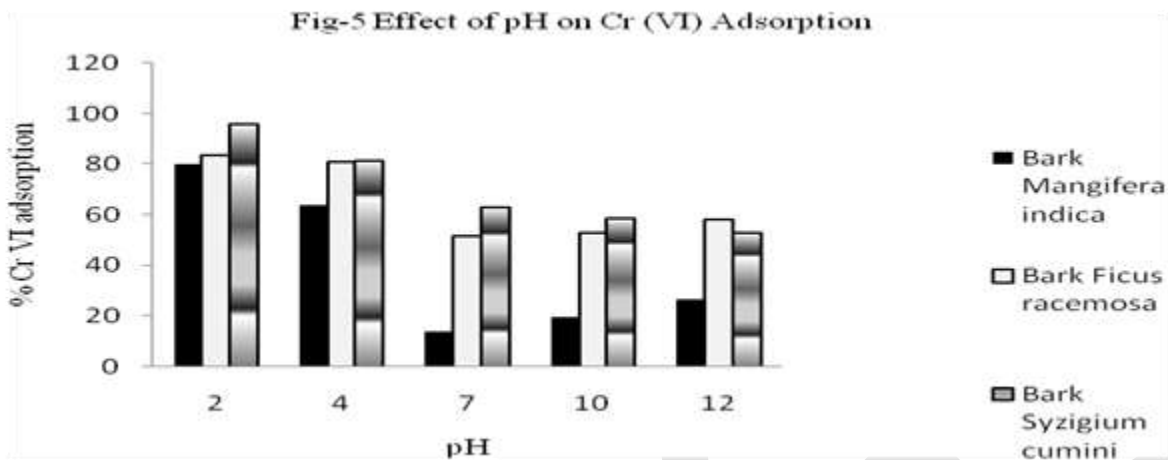

Fig-5 Effect of pH on Cr (VI) biosorption using *Mangifera indica, Ficus racemosa & Syzygium cumini* bark

Effect of Biosorbent Concentration on Cr (VI) Adsorption

The 100 mL samples of 50 mg/L hexavalent chromium concentration in 150 mL conical flasks were treated with 0.1, 0.2, 0.3, 0.4, 0.5 g of Biosorbent (*Mangifera indica, Ficus racemosa & Syzygium cumini* bark powder) maintained at room temperature 25 °C. The solutions were kept for 60 min. with gentle shaking at periodical intervals and the concentration of Cr (VI) was measured in the solution after filtering through Whatman filter paper and developing the colour using Diphenyl carbazide at 540 nm spectrophotometrically. The percentage biosorption of Cr (VI) was found maximum with biosorbent dose of 5g/l and minimum at 1g/l showing an increasing trend with increasing biosorbent doses. (Figure-6)
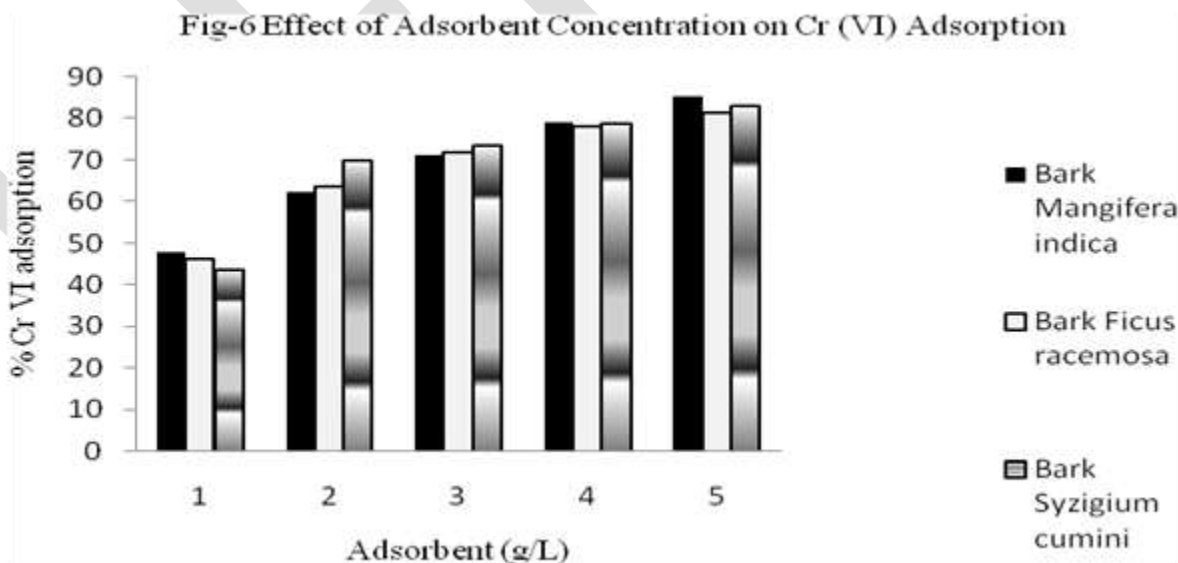

Fig-6 Effect of *Mangifera indica bark, Ficus racemosa & Syzygium cumini* bark Concentration on Cr (VI) biosorption

Adsorption Isotherms

The equilibrium of the sorption is one of the important physico-chemical aspects for the evaluation of the sorption process as a unit operation. The sorption isotherm studies are conducted by varying adsorbent dosage of 1 to 5 g/L and the initial concentration of chromium (VI) from 50 mg/L and maintaining the temp. The adsorption isotherm (qe versus Ce) shows the equilibrium between the concentration of chromium (VI) in the aqueous solution and its concentration on the solid (mass of chromium (VI) per unit mass of *Mangifera indica, Ficus racemosa & Syzygium cumini* bark powders). It is evident that adsorption capacity increases with increasing equilibrium chromium (VI) concentrations. Fig.- 7 show that the adsorption capacity of *Mangifera indica* bark increases rapidly from 0 to 18.8 mg/g for the equilibrium concentration of 0 to 15.5 mg/L. Further a gradual increase in adsorption capacity is observed with the increase in equilibrium concentration and it reaches up to 23.9 mg/g for the equilibrium concentration of 26.1 mg/L. The *Ficus racemosa* bark the linear isotherm with variable biosorbent (Fig-7) shows an increase in adsorption capacity up to 23.2 mg/g for the equilibrium concentration of 26.8 mg/L whereas in *Syzygium cumini* bark the linear isotherm with variable biosorbent (Fig-7) shows a linear increase in adsorption capacity up to 21.78 mg/g for the equilibrium concentration of 28.22 mg/L.
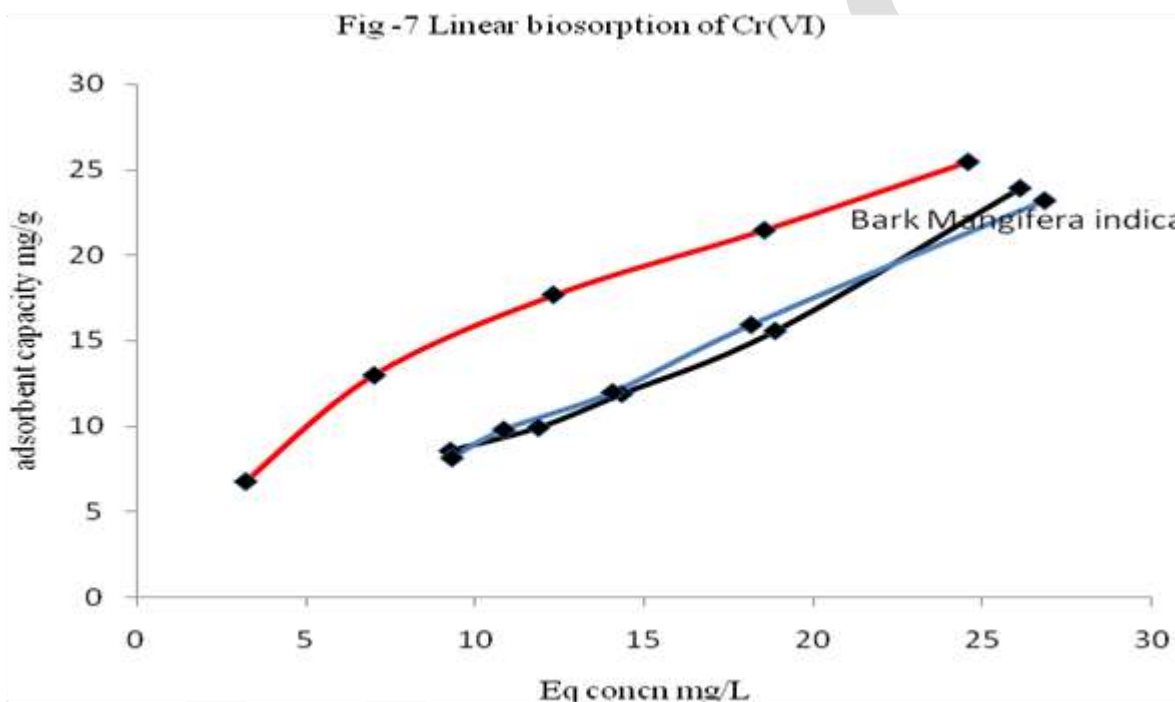

Fig -7 Linear isotherm for *Mangifera indica, Ficus racemosa & Syzygium cumini* bark biosorption of Cr(VI)

In order to model the sorption behaviour, adsorption isotherms have been studied. The adsorption process of chromium (VI) is tested with Langmuir and Freundlich isotherm models. Langmuir and Freundlich equations are given in equation (1) and (2), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \qquad\qquad (1)$$

[where b- Langmuir constant (L/mg), Ce - Concentration of Cr (VI) at equilibrium (mg/L)
qe - Amount of Cr(VI) adsorbed by the adsorbent (mg/g) and qm - Maximum adsorption capacity (mg/g)]

$$\ln q_e = \ln K_F + (1/n) \ln C_e \qquad\qquad (2)$$
[where K_F - Freundlich constant (mg/g) and n - Freundlich constant (L/mg)]

The isotherm data for *Mangifera indica, Ficus racemosa & Syzygium cumini* barks have been linearized using the Langmuir equation and shown in Fig. 8. The regression constants are tabulated in Table-1. The high value of correlation coefficient ($R^2 = 0.9877$ & 9947) indicated a good agreement between the parameters. The constant qm, which is a measure of the adsorption capacity to form a monolayer, can be as high as 13.68 & 25.9 mg/g at pH 7. The constant b, which denotes adsorption energy, is equal to 0.0568 & 0.0454 L/mg. The same data also fitted with the Freundlich equation and shown in Fig. 9. The regression constants are listed in

Table-2. The value of correlation coefficient (R^2 = 0.9407 & 9978) showed that the data confirm well to the Freundlich equation although the strength of the relationship between parameters is not as good as in the case of the Langmuir equation. The higher values (>1) of 1/n indicates the favourable condition of biosorption by the *Mangifera indica* bark by hexa valent chromium in aqueous medium.

Table No.1: Langmuir Isotherm constants for adsorption of chromium (VI) on *Mangifera indica, Ficus racemosa & Syzygium cumini* barks.

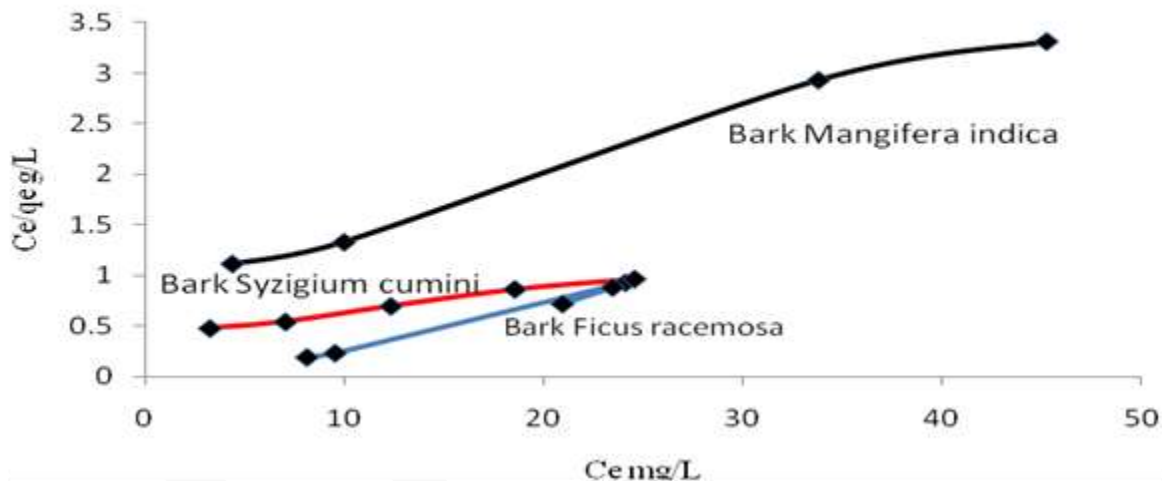| Biosorbent	Langmuir Isotherm		
	Constants		Correlation Coefficient
	Constants qm (mg/g)	b (L/mg)	(R^2)
Mangifera indica bark	13.68	0.0568	0.9877
Ficus racemosa bark	25.9	0.1715	0.9864
	25.9	0.0454	0.9947
Syzygium cumini bark	31.51	0.0879	0.9975
	25.44	0.0239	0.9911
	47.81	0.0387	0.9791
	31.92	0.0703	0.9877

Fig-8 Langmuir Isotherm for Adsorption of Cr (VI) on *Mangifera indica, Ficus racemosa & Syzygium cumini* bark

Table No.2: Freundlich Isotherm constants for adsorption of chromium (VI) on *Mangifera indica, Ficus racemosa & Syzygium cumini* barks.

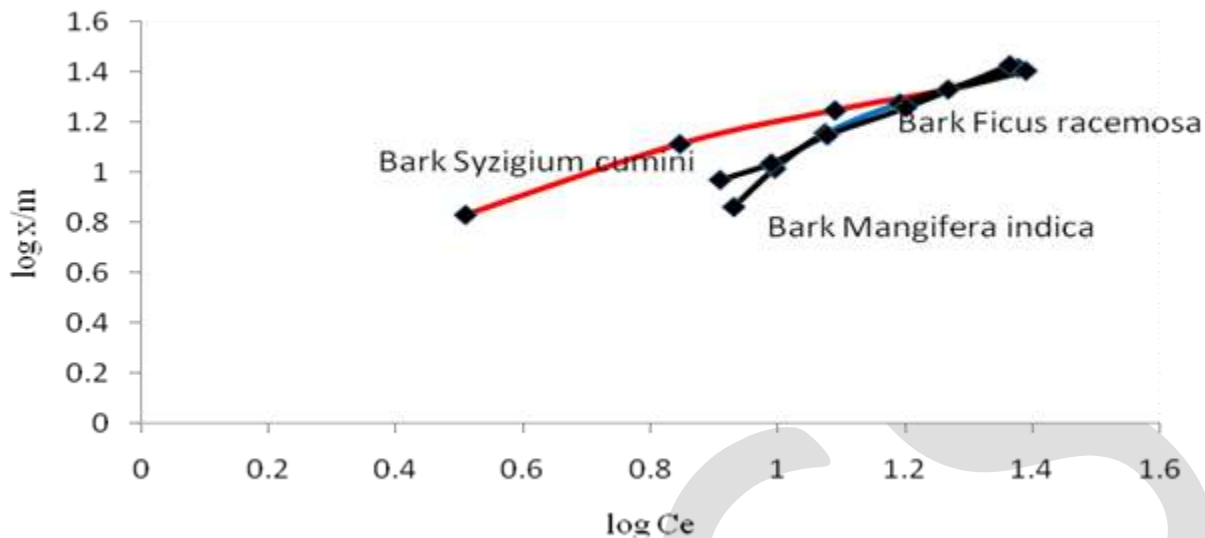| Biosorbent	Freundlich Isotherm		
	Constants		Correlation Coefficient
	K_F	1/n	(R^2)
Mangifera indica bark	0.655	1.192	0.9407
Ficus racemosa bark	1.096	1.0165	0.9978
Syzygium cumini bark	3.248	0.6402	0.9851
	1.412	0.8367	0.9705

Fig-9 Freundlich Isotherm for Cr (VI) with *Mangifera indica Ficus racemosa & Syzygium cumini* bark

FTIR spectra of *Mangifera indica* bark and biosorbent with Cr (VI)

The FTIR spectra of biosorbent (*Mangifera indica* bark) and Cr (VI) loaded was carried out using Bruker FTIR Spectrophotometer. The strong peaks observed in *Mangifera indica* bark at wave numbers 1027.23 cm^{-1} (–CN stretching vibrations of the protein fractions, Cr(VI)-O); 1604.27 cm^{-1} (C=O chelate stretching); 2362.35 cm^{-1} (vibration of –NH_2) & 3350 cm^{-1} (bonded –OH group, -NH stretching). The peaks after biosorption with Cr (VI) became more prominent and larger at 1027.36, 1611.02, 2368.11, 3329.93 cm^{-1} wave numbers respectively. The weak peaks in FTIR spectrum at 806.19 cm^{-1} (Cr (VI) compounds) & 1315.50 cm^{-1} (C=O stretching, –COOH group) were also observed in chromium loaded biosorbent. The increase in intensity of major peaks after Cr (VI) adsorption is probably due to chelating effect of chromium ion with the function group of biosorbent.

FTIR spectra of *Ficus racemosa* bark and Biosorbent with Cr (VI)

The FTIR spectra of Biosorbent and Cr (VI) loaded was carried out using Bruker FTIR Spectrophotometer. The peaks at 618, 633,644, 682, 778, 1030, 1313, 1456, 1508, 1541, 1617, 3222,3618, 3735,3822, 3858 cm^{-1} wave numbers were observed in Ficus racemosa bark while after biosorption with Cr (VI) the peaks become less prominent at 614, 641, 667, 753, 1066, 1457, 1507, 1540, 1698, 2983,3610, 3688, 3828, 3852 cm^{-1} wave numbers probably due to weak bonding with chromium (VI) atoms. The different functional groups after adsorption of Cr (VI) have shown less prominent absorption in IR spectrum.

FTIR spectra of *Syzygium cumini* bark before and after biosorption with Cr (VI)

The FTIR spectra of biosorbent (*Syzygium cumini* bark) and Cr (VI) loaded was carried out using Bruker FTIR Spectrophotometer. The strong peaks observed in *Syzygium cumini* bark at wave numbers 955.15, 1154.20 (–CN stretching vibrations of the protein fractions, Cr (VI)-O); 1395.51 (amide or sulfamide bond), 1457.05 (symmetric bending of CH_3 of acetyl moiety) 1521.54, 1540.97 (amide bond), 1647.19 (C=O chelate stretching), 2360.65 (vibration of –NH_2), 2980.33 (C-H stretching) and 3418.60 cm^{-1} (bonded –OH group, -NH stretching). The peaks after biosorption with Cr (VI) became more prominent, slight shifted and larger at 1070.90, 1249.86, 1395.92, 1457.57, 1508.38, 1542.07, 1636.87, 1699.79, 2365.91, 2980.12 and 3567.62 cm^{-1} wave numbers respectively. The increase in intensity of major peaks after Cr (VI) adsorption is probably due to chelating effect of chromium ion with the function groups of biosorbent.

CONCLUSIONS

Based on present study and experimental information derived from literature the following conclusions are made -

- Adsorbent prepared from *Mangifera indica, Ficus racemosa* and *Syzygium cumini* bark have remarkable higher biosorption capacity of 19.64 mg/g at 30 °C, 25.9 mg/g at pH=7 & 31.51 mg/g at 30 °C. respectively.
- The adsorption rate of chromium (VI) on the adsorbate prepared from *Mangifera indica* bark in the present study from aqueous solutions (5 mg/L solution and adsorbent dose of 1 g/L) is maximum for the first hour (67%) thereafter it increases very slowly up to 78% in the next four hours. Since maximum adsorption of chromium (VI) on *Mangifera indica* & *Syzygium cumini* bark

powder takes place within first hour so the equilibrium time is found to be 60 min. in the present experimental conditions. Whereas the *Ficus racemosa* bark has equilibrium time of 30 m.

- The adsorption process of chromium (VI) can be described by Langmuir isotherm and Freundlich isotherm models. However, Langmuir isotherm model shows a good agreement with the equilibrium data.
- Removal of chromium (VI) increases with increase of adsorbent dosage.
- The maximum adsorption of chromium (VI) took place in the pH range 1-3.
- The increase in temperature increases the biosorption up to 40°C, showing the chemisorptions behavior.
- The maximum adsorption takes place in 60 minutes and further increase in duration of contact time has negligible effect.
- The higher values of Freundlich constant (>1) for 1/n indicates the favourable condition of biosorption by the *Mangifera indica* bark of hexa valent chromium in aqueous medium.
- Due to higher biosorption capacity of *Syzygium cumini* bark than *Mangifera indica* and *Ficus racemosa* bark, the previous one can be used as better low cost Cr (VI) biosorbent for treating the chromium contaminated waters in the rural areas.

ACKNOWLEDGEMENT

REFERENCES:

[1] APHA, Standard Methods for the Examination of Waste and Wastewater, 19th ed., American Public Health Association, Washington, DC. ,1995.

[2] Bai R.S., Abraham E., Studies on chromium (VI) adsorption–desorption using immobilized fungal biomass. Bioresource Technology 87 (1), 17–26, 2003.

[3] Bailey S.E., Olin T.J., Bricka R.M., Adrian D., A review of potentially low-cost sorbents for heavy metals. Water Research 33 (11), 2469–2479, 1999.

[4] Basketter, David; Horev, L; Slodovnik, D; Merimes, S; Trattner, A; Ingber, A. "Investigation of the threshold for allergic reactivity to chromium". Contact Dermatitis 44 (2): 70–74, 2000

[5] Bhargava KK, Dayal R and Seshadri TR. Chemical components of Eugenia jambolana stem bark. Curr Sci., 43, 645–646, 1974.

[6] Bhatia IS and Bajaj KL. Chemical constituents of the seeds and bark of Syzygium cumini. Plant Med. 28, 347–352, 1975.

[7] BIS IS: 10500 Indian Standard Drinking Water–Specification, first revision. Bureau of Indian Standards, New Delhi, India,1991.

[8] Dakiky M., Khami A., Manassra A., Mereb, M. Selective adsorption of chromium (VI) in industrial waste water using low cost abundantly available adsorbents. Advances in Environmental Research 6 (4), 533–540, 2002.

[9] Gupta S & Babu B.V. Adsorption of Chromium (VI) by low cost adsorbent prepared from tamarind seed. Journal of Environmental Engineering and Science, Vol. 7 (No. 5), 553-557, 2008.

[10] Gupta, S. and Babu, B. V. Adsorption of Cr(VI) by a Low-Cost Adsorbent Prepared from Neem Leaves, Proceedings of National Conference on Environmental Conservation (NCEC-2006), BITS-Pilani, September 1-3, 2006, 175-180, 2006.

[11] Huang C. P. and Wu M. H. The removal of chromium (VI) from dilute aqueous solution by activated carbon, Water Research, 11, 673-679, 1977.

[12] Jianlong W., Xinmin Z. and Yi Q. Removal of Cr (VI) from Aqueous Solution by Macroporous Resin Adsorption, Journal of Environmental Science Health, 35 (7), 1211-1230, 2000.

[13] Kopanski L and Schnelle G.. Isolation of bergenin from barks of Syzygium cumini. Plant Med. 54, 572,1988.

[14] Katz, Sidney A.; Salem, H. "The toxicology of chromium with respect to its chemical speciation: A review". Journal of Applied Toxicology 13 (3): 217–224, 1992.

[15] Lotfi M., Adhoum N., Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. Separation and Purification Technology 26 (2–3), 137– 146, 2002

[16] Mauri R., Shinnar R., Amore M.D., Giordano P., Volpe A., Solvent extraction of chromium and cadmium from contaminated soils. American Institute of Chemical Engineers Journal (AIChE) 47 (2), 509–512, 2001.

[17] Namasivayam C., Yamuna R.T., Adsorption of chromium (VI) by a low-cost adsorbent: biogas residual slurry. Chemosphere 30 (3), 561–578, 1995.

[18] Namasivayam C. and Ranganathan K. Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater, Environmental Pollution, 82, 255-261,1993.

[19] Nourbakhsh M., Sag Y., Ozar D., Aksu Z., Kutsal Caglar, A comparative study of various biosorbents for removal of chromium (VI) ions from industrial waste waters. Process Biochemistry 29 (1), 1–5,1994.

[20] Orhan Y. and Buyukgungur, H. The removal of heavy metals by using agricultural wastes, Water Science Technology, 28 (2), 247-255, 1993.

[21]Ozer A., Altundogan H.S., Erdem M., Tumen F., A study on the Cr(VI) removal from aqueous solutions by steel wool. Environmental Pollution 97 (1–2), 107–112, 1997.

[22] Padilla A.P., Tavani E.L., Treatment of an industrial effluent by reverse osmosis. Desalination 129 (1–3), 219–226, 1999.

[23] Rengaraj S., Joo, C.K. Kim, Y., Yi J., Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H. Journal of Hazardous Materials 102 (2–3), 257–275, 2003.

[24] Sengupta P and Das PB.. Terpenoids and related compounds part IV triterpenoids the stem-bark of Eugenia jambolana Lam. Indian Chem Soc. 42, 255–258, 1965.

[25] Sharma D. C. and Forster C. F. A Preliminary examination into the adsorption of hexavalent chromium using Low-cost adsorbents, Bioresource Technology, 47, 257-264, 1994.

[26] Sharma A. and Bhattacharyya K. G. Adsorption of Chromium (VI) on Azadirachta Indica (Neem) Leaf Powder, Adsorption, 10, 327-338, 2004.

[27] Sharma, D.C., Forster, C.F. Column studies into the adsorption of chromium (VI) using sphagnum moss peat. Bioresource Technology 52 (3), 261–267, 1995.

[28] Singh Supriya, Tripathi Alka, Srivastava S K., Removal of Hexavalent Chromium from Contaminated Waters by Mangifera indica seed powder (Biosorption), International Journal for Scientific Research & Development, 1, (12), 2478-2484, 2014.

[29] Singh Supriya, Tripathi Alka, Srivastava S K and Prakash R. Removal of Hexavalent Chromium by Using Mangifera Indica Bark (Biosorption). International Journal of Research in Chemistry and Environment, Vol.3 (4) pp 61-67, 2013.

[30] Singh Supriya, Tripathi Alka, Srivastava S K and Prakash R. Biosorption of Chromium (VI) on Ficus Racemosa Bark Powder. International Journal of Chemistry and Applications. Volume 5 (4), pp. 237-249, 2013.

[31] Singh Supriya, Tripathi Alka, Srivastava S K and Prakash R. Biosorption Efficiency of Syzygium cumini (L.) bark for removal of Hexavalent Chromium from Contaminated Waters, Pollution Research, 33 (2) , 271-279, 2014.

[32] Srivastava A., Singh S., Prakash R. and Srivastava S.K., Impact of tanneries on ground water quality in kanchandpur area, Kanpur dehat district, U.P., Journal Ins.Pub.Health Engineers., 2, 19-26, 2013.

[33] Tanaka T.; Sueyasu T.; Nonaka G.; Nishioka I. Tannins and related compounds. XXI. Isolation and characterization of galloyl and p-hydroxybenzoyl esters of benzophenone and xanthone C-glucosides from Mangifera indica L. Chem. Pharm. Bull., 32, 2676-2686, 1984.

[34] Tan W. T., Ooi S. T. and Lee C. K. Removal of chromium (V1) from solution by coconut husk and palm pressed fibres, Environmental Technology, 14, 277-282, 1993.

[35] Tripathi Alka, Singh Supriya, Srivastava S. K., Prakash R., Evaluation of Ecotoxicological risks related to the discharge of combined industrial / sewage effluents in Unnao Industrial area, UP., Journal of Centre for Ground Water Studies. 1, 47– 53, 2013