Adsorptive Elimination of Chromium(III) and Nickel(II) from Water by Spent *Eugenia jambolana* Leaves: Isothermal and Thermodynamical Studies

Rabia Rehman[*], Jamil Anwar and Tariq Mahmud

Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan

*Corresponding author: Fax: +92 42 99230998; Tel: +92 42 99230463, Ext: 870; E-mail: grinorganic@yahoo.com

Removal of metal ions from waste-water streams is a hot issue for environmental protection. In this study, adsorption capacity of spent *Eugenia jambolana* leaves was investigated for removing chromium(III) and nickel(II) from aqueous medium. FT-IR and chemical characterization of *Eugenia jambolana* leaves helps to investigate the mechanism of adsorption. Adsorption parameters were optimized and isothermal studies were carried out. It indicated that chemisorption mode is more predominant over physiosorption of Ni(II) and Cr(III) with maximum adsorption capacity 6.003 and 3.815 mg/g, respectively. Feasibility of process is confirmed by separation factor values: 0.25 and 0.141 for Ni(II) and Cr(III) correspondingly and Gibb's free energy values: -6.971 and -5.212 KJ/mol for Ni(II) and Cr(III), respectively. Heats of adsorption for Ni(II) and Cr(III) removal by *Eugenia jambolana* leaves were -1.349 and -0.0384 KJ/mol, respectively. The results shown that *Eugenia jambolana* leaves can be used on industrial scale for removal of heavy metals.

Keywords: Chromium(III), Nickel(II), *Eugenia jambolana* leaves, Biosorption, Isothermal studies.

INTRODUCTION

Wastewater treatment for removing toxic metals is done usually by chemical precipitation, cation exchange, membrane filtration, reverse osmosis and biosorption[1-3]. The last one is studied vastly in last two decades by several scientists all over the world. Biosorption is basically a process of eradication of toxic substances by passive transfer to biosorbent from solution. It is extensively exploited as an alternative to traditional methods of removing and recovering of metals[4,5]. Cell immobilization of biomass before using for biosorption, improved its tensile strength, recycling, stability and the ease of handling. Researchers are trying waste materials from agricultural or industrial sources, having good adsorption capacity, low cost nature and availability for this purpose. Some examples are plant leaves, wheat husk, rice husk, bagasse, mango peels, banana peels, fly ash, maple sawdust, sewage waste *etc.*[6-10].

In this work, spent leaves of *Eugenia jambolana* are used for removing chromium(III) and nickel(II) from water. *Eugenia jambolana* (other names: *Syzygium jambolanum, Syzygium cumini,*Pompozia, Jamun, black plum) belongs to Myrtaceae family of plants, evergreen tropical tree, grows largely all over Asian and African countries. Its bark and seeds are used in Ayruvedic medicines. Its nut and leaves are reported to have adsorption potential for removing toxic substances like lead(II), cadmium(II), mercury (II), chromium(VI) and Brilliant green dye[11-14].

The metals selected for study here are chromium(III) and nickel(II). These are essential elements for various biological activities of organisms like Cr(III) is important for sugar and lipid metabolism, whereas Ni(II) is essential for increasing iron absorption and treating osteoporosis. It is found in nucleic acids, where it is involved in protein structure development. It also supports the production of prolactin which is essential for mammals breast milk production. But excess quantity of Cr(III) and Ni(II) is toxic leading to various diseases *e.g.*, nickel dermatitis allergy, carcinogenic and mutagenic activities, skin rashes, bronchitis, *etc*. They are usually found in waste water streams of electroplating activities, steel foundries, printing, batteries, vehicle industries, porcelain and chemical industries[15-19]. Permissible limits of Cr(III) and Ni(II) are 0.05 and 0.5 mg/L, respectively, in drinking water[20,21]. So their removal from waste streams is crucial before discharging them into main water reservoirs.

EXPERIMENTAL

$CrCl_3.6H_2O$, $NiSO_4.6H_2O$, HCl, NaOH and NaCl were obtained from Merck (Germany). Atomic absorption spectrometer (Perkin Elmer AAnalyst 100, equipped with air-acetylene burner) and FT-IR spectrometer (Perkin Elmer RX-I) were used.

Biosorbent preparation and characterization: *Eugenia jambolana* leaves (EGL) were collected from home institute.

They were washed and dried in sunlight for 4-7 days and then in oven at 70 °C for 4 h. Then they were ground and sieved through 60 mesh (ASTM). The fine powder was stored in plastic bottles after labeling, till further use. FT-IR spectrum of *Eugenia jambolana* leaves powder was recorded for surface characterization and resulting vibrational frequencies of specific functional groups were analyzed and presented in Table-1. Various physiochemical parameters like carboxylic acid content, lactones and basic sites contents (by Boehm titration), moisture contents, pH, ash content and iodine number were determined using standard methods as described by Ekpete and Horsfall[22] (Table-2).

TABLE-1
CHARACTERISTIC FT-IR FREQUENCIES OF
Eugenia jambolana LEAVES

Functional groups assignment	Band frequencies (cm^{-1})
ν(N-H)	3291 (m), 1612 (m)
ν(C-H) of -CHO	2917 (w)
ν(O-H)	1023 (m)
ν(-NCS), (-NCO) or (-CN)	2354.3 (w)
ν(C=O)	1241.6 (s)
ν(C-N)	1023 (m)

TABLE-2
PHYSIOCHEMICAL ANALYSIS OF *Eugenia jambolana* LEAVES

Physiochemical parameters	Quantification
Carboxylic (acidic function) (mmol)	1.986
Phenol (mmol)	0.003
Lactones (mmol)	0.001
Basic sites (mmol)	1.98
pH	5
Iodine value (mg g^{-1})	8.37
Moisture contents (%)	7.0
Ash contents (%)	6.1
Volatile organic components (%)	27.6
Bulk density (g/cm^3)	0.895
Dry density (g/cm^3)	0.292

Synthetic waste water preparation and analysis of metal ions: Stock solutions (1000 mg/L) of Cr(III) and Ni(II) were made separately by mixing 3.03 g of $CrCl_3.6H_2O$ and 5.08 g of $NiSO_4.6H_2O$ in small amount of de-ionized water and diluting up to 1 L. Further they were diluted according to the requirements of experimental conditions.

Adsorption studies: Different parameters were investigated by varying adsorbent amount (0.2-1.8 g), contact time, (10-90 min), initial pH of solution (1-8), agitation speed (50-250 rpm) and temperature (20-70 °C) using 50 mL of 50 ppm (C_o) metal ion solutions (V) separately, at 25 ± 1 °C. pH was adjusted with 0.01 M HCl/NaOH according to requirement using pH meter (HANNA pH 211). After each experiment, solutions were filtered and remaining metal ions 'C_e' concentration was determined by AAS working at 357.9 nm for chromium and for nickel at 232 nm. For isothermal studies, stock solutions of Cr(III) and Ni(II) were diluted in range of 30-80 ppm separately and optimized conditions of all above parameters were applied correspondingly[23].

Mathematical data evaluation: The percentage removal of metal ions was determined by eqn. 1:

$$\text{Removal of metal ions (\%)} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Langmuir parameters were calculated by regression analysis of eqn. 2:

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \qquad (2)$$

Freundlich parameters were calculated by regression analysis of eqn. 3:

$$\log q = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

Temkin parameters were calculated by regression analysis of eqn. 4:

$$q = B_T \ln C_e + B_T \ln K_T \qquad (4)$$

Adsorption capacity 'q' was determined by eqn. 5:

$$q = \frac{(C_o - C_e)V}{m} \qquad (5)$$

$$R_L = \frac{1}{(1 + bC_o)} \qquad (6)$$

Thermodynamic parameter 2$\Delta G°$' was determined by eqn. 7:

$$\Delta G° = -RT \ln K \qquad (7)$$

In these equations, 'q' (mg/g) is the amount of metal ions removed by *Eugenia jambolana* leaves, 'q_m' (mg/g) and b (L/g) are Langmuir parameters, 'K_F' ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) and 'n' are Freundlich constants, heat of adsorption is 'B_T' = RT/b, 'T' is temperature (Kelvin), 'R' is gas constant (8.314 J/mol), 'K_T' is the equilibrium binding constant (L/mg), '$\Delta G°$' is Gibb's free energy (KJ/mol) and 'K' = 1/b[24-29].

RESULTS AND DISCUSSION

Surface characterization of *Eugenia jambolana* leaves: FT-IR analysis of *Eugenia jambolana* leaves revealed that it contains several functional groups *e.g.*, -OH, -CO, -NH and -COOH that can act as possible adsorption sites (Table-1). The bands at 2917 cm^{-1} were due to methylene ($-CH_2-CH_2-$) group stretching vibrations. The band at 1242 cm^{-1} was ascribed to ester, ethers and/or phenol groups. Vibrational peaks between 2300-2000 cm^{-1} was assigned to -NCS, -NCO or -CN[14]. Physio-chemical analysis of *Eugenia jambolana* leaves given in Table-2 showed decreased levels of moisture, ash and volatile matter contents, demonstrating that the particle density is quite small and this biomaterial should be an efficient raw material as an adsorbent. Iodine value is indicating that sufficient amount unsaturated compounds are present in *Eugenia jambolana* leaves. The type/concentration of surface functional groups of *Eugenia jambolana* leaves were found by the Boehm titration procedure. Strongly acidic carboxylic sites are neutralized by $NaHCO_3$, whereas those neutralized by Na_2CO_3 are thought to be lactonic and carboxylic sites which can bind metal ions during adsorption process. The weakly acidic phenolic sites only react with NaOH. Surface basic group's pyrones and chromenes were neutralized by HCl, which can chelate metal ions[22].

Adsorption parameters optimization: Batch adsorption process had been carried out for the removal of Ni(II) and Cr(III) by *Eugenia jambolana* leaves as an adsorbent. By utilizing the adsorption properties of *Eugenia jambolana* leaves these heavy metals had been removed from their aqueous solution and different parameters had been studied. Adsorption is a complex phenomenon in which metallic species can be deposited on *Eugenia jambolana* leaves through various process *e.g.* complexation, ion-exchange, precipitation, chelation *etc*. The rapid uptake of Cr(III) and Ni(II) from their aqueous solution has suggested that the metal binding has occurred due to cell wall structure of the *Eugenia jambolana* leaves and not due to any cellular process, because it is dependent on chemical make-up of cell wall and not on metabolic activities within plant cells.

Fig. 1 shows that in the case of Cr(III) adsorption increases with an increase in adsorbent amount to some extent and after reaching equilibrium it became constant whereas in the case of Ni(II) the adsorption decreases after the equilibrium has been established. For Cr(III) minimum adsorption the dose of 1.4 g to maximum adsorption value of 80.16 % for dose of 0.6 g. For Ni(II) minimum adsorption was 77.44 % for the dose of 0.2 g to maximum adsorption value of 86.86 % for dose of 0.8 g. More adsorption sites are vacant at the beginning, so adsorption rate increases gradually, then decreases. It is also observed that adsorption with high dose of adsorbent need less time interval to reach equilibrium.
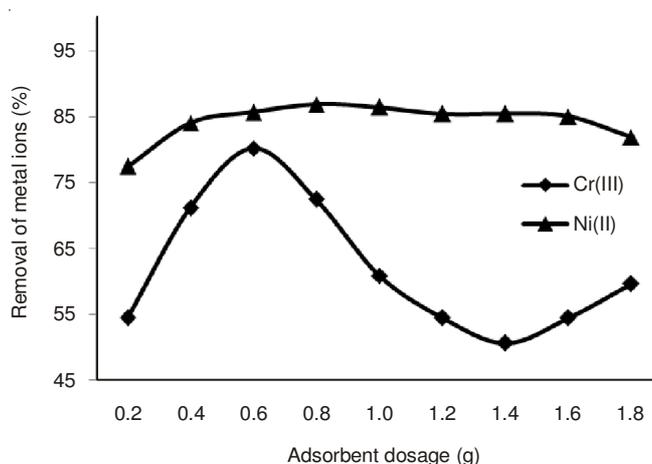
Fig. 1. Adsorbent dose effect on Cr(III) and Ni(II) adsorptive removal from water by *Eugenia jambolana* leaves

Fig. 2 shows the effect of contact time on adsorption for Cr(III) and Ni(II). For Cr(III), minimum removal was 59.56 % for contact time of 5 min and maximum removal was 84.03 % for contact time of 25 min. For Ni(II) minimum removal was 77.64 % for the time of 5 min and maximum removal was 90.47 % for contact time of 15 min. In start of adsorption process, removal occurs rapidly as soon as metal ions and biosorbent came into contact, because metal ions have more time for making complex with it. But after that metal ions needs time for finding out more active sites for binding[27,28].

Fig. 3 showed that pH affects adsorption processes of metal ions considerably. As the pH rises, removal efficiency of adsorbent increases and the best results are obtained at pH
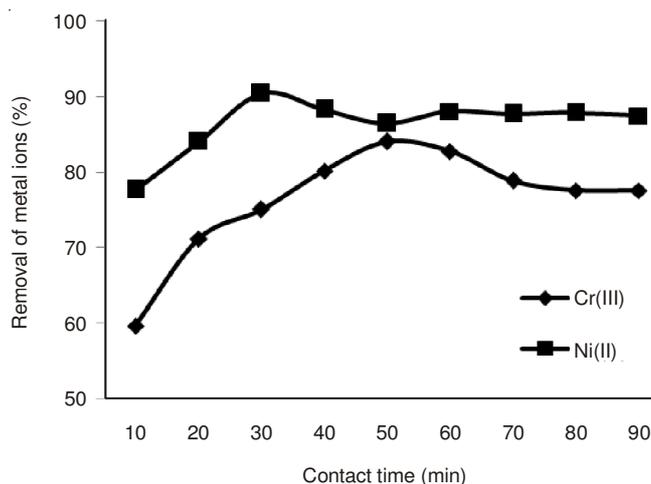
Fig. 2. Contact time effect on Cr(III) and Ni(II) adsorptive removal from water by *Eugenia jambolana* leaves
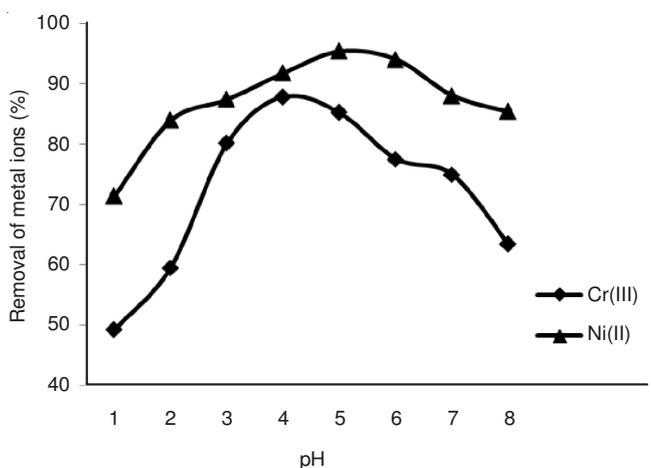
Fig. 3. Solution pH effect on Cr(III) and Ni(II) adsorptive removal from water by *Eugenia jambolana* leaves

= 4. For Cr(III), minimum removal was 49.25 % at pH = 1 and maximum removal was 87.89 % at pH = 4 *i.e.*, the adsorption takes place in acidic media. It is found that at pH lower than 4; chromium removal is inhibited possibly as a result of competition between hydrogen and Cr(III) ions. For Ni(II), optimum adsorption occurred at pH = 5 *i.e.*, in acidic media. Minimum removal was 71.43 % at pH = 1 and maximum removal efficiency was 95.48 % at 5 pH. Adsorption takes place as the carboxyl functional groups are deprotonated and provide active sites for the binding of metal ions. At high pH (greater than 8.5), precipitation occurred due to the formation of hydroxides, making accurate sorption studies difficult.

Effect of agitation speed on adsorptive removal of metal ions by *Eugenia jambolana* leaves was shown in Fig. 4. By increasing shaking speed, adsorption increases. If it is slow, the adsorbent accumulates instead of spreading in solution and binding sites are buried under the above layers of adsorbent powder. So adsorption occurs by above layers and suppressed layers do not involve in it. Increase in adsorption with agitation speed is also due to the fact that adsorbent is thoroughly mixed in water at high speed and as a result more metal ions and adsorbent came into contact due to formation of very fine suspension and thus, removal efficiency increases. The minimum

TABLE-3
LANGMUIR PARAMETERS FOR Cr(III) AND Ni(II) ADSORPTIVE REMOVAL FROM WATER BY *Eugenia jambolana* LEAVES

Metal ions	Slope	Intercept	R^2	q_{max} (mg/g)	b (L/g)	R_L	$\Delta G°$ (KJ/mol)
Ni(II)	2.153	0.262	0.987	6.003	0.060	0.25	-6.971
Cr(III)	2.769	0.167	0.982	3.815	0.122	0.141	-5.212
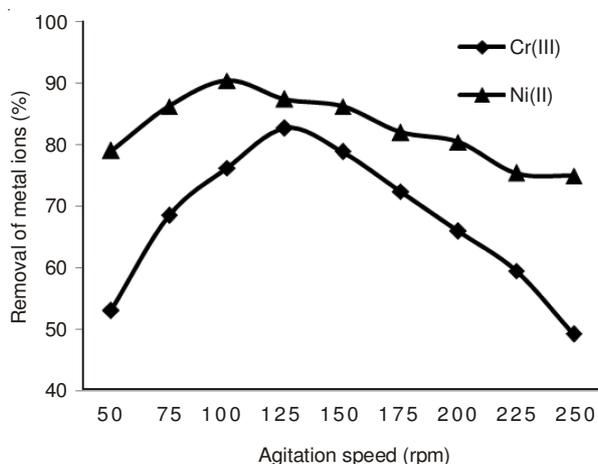
Fig. 4. Agitation effect on Cr(III) and Ni(II) adsorptive removal from water by *Eugenia jambolana* leaves

removal of Cr(III) was 49.25 % at 250 rpm and maximum removal was 82.74 % at 125 rpm. This indicates that shaking rate should be satisfactory for ensuring that entire adsorption sites are made readily available for Cr(III) uptake. For Ni(II), minimum removal was 75.04 % at 250 rpm and maximum removal was 90.47 % at 100 rpm. So, agitation speed of 125 and 100 rpm were found optimum for both Cr(III) and Ni(II) removal, respectively by *Eugenia jambolana* leaves. But at greater speed, removal efficiency of *Eugenia jambolana* leaves decreased as less contact occurred between metal ion solution and adsorbent[29].

Temperature effects adsorption processes, because they are usually endothermic. Using agro-waste material, this factor gains more importance, because at higher temperature degradation of biopolymers present in plant materials occurred. Sometimes it is beneficial, as more adsorption sites are created, but usually it is not favorable, because it decreases shelf life of biosorbent[17-19]. Fig. 5 is showed that the maximum adsorption of Cr(III) occurred at 40 °C and of Ni(II) at 30 °C.
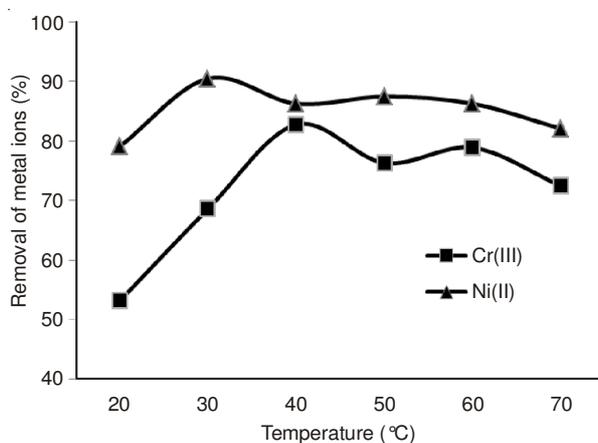
Fig. 5. Temperature effect on Cr(III) and Ni(II) adsorptive removal from water by *Eugenia jambolana* leaves

Isothermal and mechanistic studies: For determining mechanism of adsorption, isothermal parameters are investigated using three models, namely: Langmuir, Freundlich and Temkin and their respective values are tabulated in Tables 3-5, respectively. Comparison of correlation coefficient 'R^2' values indicated that Freundlich parameters is more followed by both metal ions, as compared to other two models, indicating that multilayer physiosorption occurred more as compared to monolayer chemisorption. Maximum adsorptive removal of Ni(II) and Cr(III) are 6.003 and 3.815 mg/g of *Eugenia jambolana* leaves (EGL). Comparing these values with other reported adsorbent values indicated that *Eugenia jambolana* leaves has great potential to be used as adsorbent, as clear from Table-6. Langmuir isotherm constant 'b'(L/g) values for Ni(II) and Cr(III) is: 0.060 and 0.1217 L/g. They were used to calculate separation factor values, R_L and Gibb's free energy $\Delta G°$. The R_L values between 0-1 means favorable adsorption. Negative values of Gibb's free energy indicated the spontaneity of the process. Freundlich model constant 'n' values for Ni(II) and Cr(III) are 1.82 and 2.448, respectively. Temkin parameters K_T values for Ni(II) and Cr(III); 1.556, 0.916; depicted satisfactory adsorption potential of *Eugenia jambolana* leaves. Also heat of sorption B_T values were -1.349 and -0.0384 for Ni(II) and Cr(III) correspondingly suggested weak chemical interaction between metal ions and *Eugenia jambolana* leaves. The constants 'n' and 'B_T' values lesser than 8 point out weaker interaction between metal ions and adsorbent, favoring physiosorption mode of adsorption[25-29].

TABLE-4
FREUNDLICH PARAMETERS FOR Cr(III) AND Ni(II) ADSORPTIVE REMOVAL FROM WATER BY *Eugenia jambolana* LEAVES

Metal ions	Slope	Intercept	R^2	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n
Ni(II)	0.549	0.204	0.995	0.625	1.82
Cr(III)	0.408	0.104	0.987	0.787	2.448

TABLE-5
TEMKIN PARAMETERS FOR Cr(III) AND Ni(II) ADSORPTIVE REMOVAL FROM WATER BY *Eugenia jambolana* LEAVES

Metal ions	Slope	Intercept	R^2	B_T (KJ/mol)	K_T
Ni(II)	1.556	1.349	0.984	-1.349	1.556
Cr(III)	0.916	0.0384	0.986	-0.0384	0.916

Conclusion

It is found that *Eugenia jambolana* leaves can efficiently remove Cr(III) and Ni(II) ions from water. Optimized conditions for Cr(III) are: 0.6 g adsorbent dose, 25 minutes contact time, 4 pH, 125 rpm agitation speed and 40 °C temperature, and for Ni(II) are: 0.8 g adsorbent dose, 15 min contact time, 5 pH, 100 rpm agitation speed and 30 °C temperature. Hence it is concluded that *Eugenia jambolana* leaves are the efficient

TABLE-6
MAXIMUM ADSORPTION CAPACITY OF REPORTED ADSORBENTS FOR REMOVING Cr(III) AND Ni(II) FROM WATER[17-29]

Cr(III)		Ni(II)	
Adsorbent	q_{max} (mg/g)	Adsorbent	q_{max} (mg/g)
Poplar tree	5.52	Fly ash	0.683
Spruce	0.30	Granular activated carbon	1.49
Straw Sorghum	6.96	Cashew nut shell	18.868
Polyalthia longifolia leaves	1.87	*Pinus sylvestris* cone	3.12
Test of sea urchin	15.46	*Aspergillus niger*	1.1
Talinum triangulare (water leaf)	40	Rice hull	5.58

adsorbent, as these show high efficiency for the removal of Cr(III) and Ni(II) from aqueous solutions. The maximum adsorption capacity (q_{max}) for Ni(II) and Cr(III) obtained from Langmuir isotherm is 6.0024 and 3.815 (mg of metal/g adsorbent). So, it is concluded that *Eugenia jambolana* leaves are the efficient adsorbent for the removal of Cr(III) and Ni(II) from wastewater in the order Ni(II) > Cr(III). Freundlich adsorption isotherm model shows linearity for removal of both the metals indicating the multi-layer physiosorption is dominant over chemisorption. Thermodynamic values favour the spontaneity of process. So, *Eugenia jambolana* leaves can be effectively employed on larger scale metal ion removal from wastewater, as it is cheap and easily available from indigenous sources of Asian countries.

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