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An efficient of *Sansevieria trifasciata* plant as biosorbent for the treatment of metal contaminated industrial effluents

Saadia R. Tariq Farah Iqbal Yusra Safa

Department of Chemistry, Lahore College for Women University, Lahore, Pacistan.

E-mail: saadiartariq@yahoo.com

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Abstract:

Sansevieria trifasciata was studied as a potential biosorbent for chromium, copper and nickel removal in batch process from electroplating and tannery effluents. Different parameters influencing the biosorption process such as pH, contact time, and amount of biosorbent were optimized while using the 80 mm sized particles of the biosorbent. As high as 91.3 % Ni and 92.7 % Cu were removed at pH of 6 and 4.5 respectively, while optimum Cr removal of 91.34 % from electroplating and 94.6 % from tannery effluents was found at pH 6.0 and 4.0 respectively. Pseudo second order model was found to best fit the kinetic data for all the metals as evidenced by their greater R^2 values. FTIR characterization of biosorbent revealed the presence of carboxyl and hydroxyl groups on its surface that were responsible for metal uptake. The data for Cr removal from both the effluents was best fitted to Freundlich isotherm. Moreover, 84% biosorbent was recovered on desorption.

Key words: Biosorption, industrial effluents, Freundlich isotherm, Langmuir isotherm, *Sansevieria trifasciata*

Introduction:

The sustainability of human race largely depends on water, but the burgeoning growth of various industries has put the quantity and quality of available water resources at stake. These industries produce voluminous amounts of metal laden effluents and discharge them indiscriminately to nullahs, ditches, open lands, sewers and rivers. After percolation through the soil, the hazardous heavy metals ultimately find their way to the groundwater that is the only drinking water source available to

the populations of arid regions. Thus in order to ensure the sustainability of water resources, there is an urgent need to look for an economic treatment methodology for the effluents emanating from the industries [1]. Numerous techniques have been developed to cope with the situation, such as membrane technologies chemical precipitation, and adsorption onto bentonite and activated carbon, but they suffer from inherent economical or technical constraints that have limited their use [2-8]. Biosorption has recently emerged as the potential alternative for the remediation of metal laden industrial or municipal wastewaters due to its high detoxifying potential, low operation costs, no nutrient requirements, production of little biological sludge and ease of availability of various biomaterials [9, 10]. Moreover, under normal pressure and temperature conditions this process may be carried out efficiently at a rapid pace.

Recently, numerous biomaterials have been tested for their potential for the abatement of toxic metals like Cu, Al, Ni, Hg, Cr, Fe, Cd, Zn and Pb from aqueous media; these include barks, seed husks, leaves, peels and pulp of vegetables and fruits etc., [1, 11-17]. But the challenge for selecting an abundantly available and inexpensive biomass with better metal adsorption potential and selectivity lies ahead [18]. Sansevieria trifasciata belonging to Ruscaceae family is an angiospermic monocot. It is commonly known as snake plant. It has stiff, erect and succulent leaves that are excellent air cleaners as they absorb various organic chemicals such as xylene, toluene and formaldehyde from the air and are capable withstanding of diverse environmental conditions [18, 19]. In fact the presence of different functional groups such as carboxyl, amino and hydroxyl etc. on the surface of leaves of Sansevieria trifasciata facilitate the biosorption process by binding with various metals present in the effluents.

In view of these considerations, the present study focused on the use of *Sansevieria trifasciata* biomaterial for the removal of heavy metals like Cu, Ni and Cr present in different industrial effluents. Various process parameters such as biosorbent dose pH, shaking time, and particle size of biosorbent were optimized for large scale applications. The regeneration of the

biosorbent for reuse was another objective of the study.

Materials and Methods: Instrumentation

The concentration of metal ions in the effluent samples were determined by using Hitachi Atomic Absorption Spectrophotometer model AA-5000. The surface morphology of biosorbent was studied bv Agilent **FTIR** spectrophotometer. The pН and electrical conductivities of the samples were determined by using the WTW, Inolab-720 pH meter and conductivity meter respectively.

Biosorbent/biosorbate preparation

Sansevieria trifasciata leaves were obtained from the Botanical garden of Lahore College for Women University, Pakistan. These were rinsed thoroughly with doubly distilled water (DDW) and dried at 80°C for 96 hours in an oven. The dried biomass was ground in a food Processor and then sieved to get the biomass particles of different sizes i.e. 60, 80 and 100 mm.

The wastewater samples with high contamination of Cr and Ni were obtained from the leather industry and electroplating units operative in Sialkot, Pakistan. For the copper remediation studies, aqueous solution of Cu prepared under acidic conditions by dissolving 3.93 g of CuSO₄.5H₂O in one dm³ of DDW was used. All the effluents were collected in 2.5 L capacity, prewashed and dried PET bottles which were transferred immediately to lab. for analysis. Working solutions of different concentrations of Cu (II) were prepared from stock solution after appropriate dilution.

These effluents were analysed for the determination of various physicochemical parameters such as, EC, pH, sulphate, nitrate and chloride by using the standard methods [20]. Analytical grade reagents procured from E-Merck (Germany) were used for the present study. Stock metal solutions of 1000 mg/L concentration for use in metal estimation by atomic absorption spectroscopy were also obtained from E-Merck.

Batch biosorption studies

The batch biosorption experiments were using performed by Sansiviera trifasciata biomass and various parameters that influence the biosorption process i.e. time of contact, pH, dose of biomass and mesh size were optimized. The amount of the metal ions in the effluent samples before and after biosorption process the were determined. FTIR spectroscopy revealed the presence of various chemical functional groups present on the biosorbent's surface that play an important role in the biosorption of metals.

To study the influence of pH on biosorption process, 10 mL of respective effluent was shaken with certain amount of biosorbent for 1 h at room temperature $(25\pm2^{\circ}C)$ while maintaining the pH in varying range of 2-9. pH was therefore noted for the biosorption of Cr (total), Cu (II) and Ni (II) present in synthetic, Ni plating, leather effluent and chrome plating effluents.

To determine the effect of dose of biosorbent on metal removal potential, 10-100 mg portions of biomass were added to the Erlenmeyer flasks containing 10 mL of effluent solution that had been maintained at an optimum pH and agitated at 200 rmp for one hour at $25\pm2^{\circ}$ C. The filtrate thus obtained was analyzed by AAS for the estimation of metal and the optimum biosorbent dose was recorded.

The effect of time of contact on biosorption phenomenon was determined by changing the agitation time from 10-240 minutes under optimum dose of biosorbent and pH. Similarly, the 60, 80 and 100 mm sized particles of biosorbent were used to study the effect of particle size of biosorbent on biosorption potential of Sansevieria trifasciata.

The biosorbents efficiency (E) for the removal of metals was calculated by using the equation 1.

$$E = \frac{(C_i \times C_e) \times 100}{C_i} \qquad \dots (1)$$

Where C_i = initial metal concentration, C_e = metal level at equilibrium. The capacity for metal uptake of biosorbent (q) was calculated by ($C_i - C_e$) / M, Where q in units of mg/g is the metal uptake by biosorbent, M is the biosorbent dose in g and V in units of L represents the volume of the effluent.

Desorption Studies

In order to study the potential of the biosorbent for repeated use, the desorption experiments were performed. To this effect, the metal loaded biosorbent obtained after biosorption was treated with dilute hydrochloric acid solution (2.0 M) for 2hrs. The contents were filtered and the filtrate obtained was used to determine the desorbed metal ions. The regenerated biosorbent was washed thoroughly with DDW and reused [21].

Kinetic and Equillibrium Studies

The kinetics of biosorption was studied by using the Lagergren First order and pseudo second order models [22, 23] as elaborated in equations 2 and 3.

$$log(q_e - q_t) = \frac{logq_e - k_1 t}{2.303} \quad ... (2)$$
$$\frac{t}{q_t} = \frac{1}{k_2} \times q_e^2 + \frac{t}{q_e} \quad ... (3)$$

where q_t and q_e are the biosorbate concentrations at time t and at equilibrium in units of mg g⁻¹, t = time in minute, k_1 and k_2 are reaction constant in units of min⁻¹ and g/ mg.min. respectively.

The biosorption equillibrium was studied by applying the Langmuir and Freundlich isotherms as given in equations 4 and 5.

$$\frac{C_e}{q_e} = \frac{1}{q_{max.}} \times \frac{K_L + C_e}{q_{max.}} \qquad \dots (4)$$
$$log q_e = log K_f + \frac{1}{n} \times log C_e \qquad \dots (5)$$

Where K_L in units of L /mg is the constant for biosorption, q_{max} (mg g⁻¹) is monolayer biosorbent capacity, 1/n and K_f are the Freundlich constants, the separation factor, R_L describing the distinct characteristics of Langmuir model was evaluated as:

$$R_L = \frac{1}{1 + K_L + C_I} \quad ... (6)$$

Where C_i = initial metal concentration of adsorbate and K_L = Langmuir constant.

Results and Discussion:

The current study deals with the application of Sansevieria trifasciata for the removal of metals present in industrial effluents specially those emanating from electroplating industry and tannery industry that contain large amounts of Cr and Ni. The study also focused on the Cu(II) biosorption onto the novel biosorbent. The details of the results of the study are provided below: effluents from tannerv The and electroplating industry exhibited highly acidic nature with mean pH values of 3.14 and 3.05 respectively while effluent from synthetic Cu and Ni plating industry were neutral in nature. These effluent samples also exhibited enhanced Cl^{-1} , SO_4^{-2} and NO_3^{-1} levels surpassing the NEQS, Pakistan. Cr in tannery effluents was found to be 163 mg/L, while Cr in the electroplating effluent was found to be 279 mg/L. Ni

concentration in electroplating industry effluent was 141mg/L on average.

1. Effect of pH

pH of the medium is one of the important parameters that influences the adsorbent-adsorbate interactions, thus for the present study as well the optimization of pH of biosorption process was carried out and the corresponding data is provided in Figure 1. For biosorption of Cr present in electroplating effluent, the optimum pH was found to be 6 that yielded 91.78 % removal efficiency. When the matrix was changed from electroplating industry effluent to tannery effluent, the optimum pH was shifted to 4. Ni Biosorption from electroplating effluent was also found to be optimum at a pH 6. while a 92.7 % removal potential of biomass was exhibited at an optimum pH of 4.5 for synthetic Cu solution. At pH greater than 7, an abrupt increase in metal removal was observed.

The metal ions diffuse from the bulk solution to active sites of the biomass where they bind through different functional groups such as hydroxyl, carboxylate and amino [24]. An increase in metal uptake with an increase in pH can be explained on the basis of surface complexation theory that is based on a decreased competition between the metal ions and protons for the active sites. At pH approaching to 7 most of the active sites of the biomass have been occupied so the biosorption is reduced but on further increasing the pH the metal precipitation as hydroxides is increased.



Fig. 1. Biosorption efficiency of *Sansevieria trifasciata* for metals as a function of pH.

2. Effect of dose of biomass

The variation in biosorption capacity of *S. trifasciata* with the dose of biosorbent is depicted in Figure 2. The figure depicted that Cr removal efficiency from electroplating effluent was increased up to 63.6 % with an adsorbent dose of about 0.10g/L. A maximum Ni removal efficiency of 93.9 % was observed at this biosorbent dose of 0.10 g/L. A

similar metal uptake trend was followed by Cu present in synthetic aqueous solution and Cr (tannery effluents) with some changes in amount of biosorbent and relevant variations in metal uptake. For the Cr present in the tannery effluent, an optimum biosorption of 96.59 % was observed at 0.01g/L dose while 61.3% of Cu was removed with this dose of 0.10 g/L.



Fig. 2. Effect of dose of *Sansevieria trifasciata* biomass on biosorption of metals. 3. Effect of contact time

The data for the effect of time of contact between the adsorbent and adsorbate on the biosorption process is depicted in Figure 3. For the Cr biosorption from electroplating industry effluent, the optimum time observed was 10 mintues where a 45.49% metal removal was recorded. The biosorption efficiency was found to decrease beyond the optimum period. While an optimum agitation interval of 80 minutes was required for Cr removal from tannery effluents. Similarly, an optimum time of 20 minutes was required for optimal Ni removal from the electroplating industry effluent. For the removal of Cu from aqueous synthetic effluent, the optimum removal efficiency of *S. trifasciata* after an agitation time of 40 minutes was found to be 59%. Shaking the biosorbent

and biosorbate together ensures efficient interaction between them. But once the equilibrium is reached rate of desorption increases with time. This is illustrated due to more available sorption sites in the beginning of biosorption experiment. With the increasing time, more and more metal ions occupy the sorption sites; hence, adsorption is increased. At equilibrium state, maximum metal ions place. adsorption takes Bevond equilibrium, the complete coverage of sorption sites with metal ions leads to an increase in desorption which is quite in agreement previous studies [25-27].



Fig. 3 Variation in biosorption efficiency of *Sansiviera trifasciata* as a function of shaking time

4. Effect of particle size of biosorbent

In order to study the effect of particle size of biomaterial on the removal of metals, three different particle sizes i.e., 60, 80 and 100 mm were used. It was found from the results of the study that particle size of 80 mm entailed an optimum metal removal from different industrial effluents (Figure 4).

5. Equilibria studies of biosorption

Freundlich and Langmuir equilibrium isotherm models were used to investigate the biosorption potential of S. trifasciata for Cr, Cu and Ni present industrial effluents. Various in parameters of these models such as K_f, n, q_{max} and K_L were evaluated by using the regression analysis that also helped in the determination of slope and intercept values.



Fig.4. Effect of particle size of *Sansevieria trifasciata* biomass on the biosorption of metals.

The linearized form of Freundlich model was used to study the biosorption of different metals and R^2 values were evaluated by using the regression analysis. These linear equations were used to determine the values of K_f and n, that are given in Table 1. The values of n for the Cr biosorption from the tannery effluent and electroplating industry effluent were found to be 0.0435 and 0.0059 respectively, while an n-value of 0.0902 was recorded for Ni removal from the electroplating industry effluents. Similarly, Cu biosorption onto biomaterial yielded a nvalue of 0.6703. All these n values were lower than one that depicted а heterogeneous surface of biosorbent.

The sorption parameters of Langmuir model were determined by using the

linearized Langmuir equation and by ploting Ce vs Ce/qe. The slope and intercept of this linear plot yielded Langmuir parameters i.e. q_{max} and K_L (Table 1). The separation factor R_L was also determined and its values for all the three metals was found to be lower than 1 that pointed towards the fact that adsorption process was affirmative [28]. The R^2 values obtained for Langmuir isotherm for Cr biosorption from either of the two effluents were much higher as compared to those provided bv Freundlich model, thus Langmuir model better fitted this data set. For the biosorptive removal of Ni and Cu, Freundlich model was better fitted the data as evidenced by higher R^2 values provided by Freundlich model.

 Table 1. Parameters of Langmuir and Freundlich isotherms for metal uptake by

 Sansevieria trifasciata.

Langmuir model					Freundlich model		
Metal	q _{max}	KL	\mathbf{R}^2	R _L	n	K _f	\mathbf{R}^2
Cr (plating)	277.7	0.00168	0.9582	0.00043	0.0059	3.1174	0.4564
Cr (Tannery)	178.5	0.008	0.9361	0.00026	0.0435	3.6505	0.4095
Ni (plating)	147	0.016	0.4027	0.00098	0.0902	3.1306	0.5962
Cu (Synthetic)	57.1	0.02	0.5725	0.0052	0.6703	3.2753	0.8538

6. Kinetics of Biosorption

First order and pseudo second order models were found to fit the biosorption data. The corresponding data is provided in Table 2. The results of the study exhibited pseudo second order model to best fit the data for all the three selected metals present in various effluents as evidenced by greater R^2 values obtained for this model.

Table 2. Lagergren first order and pseudo second order kinetic parameters for the biosorption of metals on *Sansevieria trifasciata* biomass.

	1st order			Pseudo second order		
Metal	K ₁	q _{max}	\mathbf{R}^2	k ₂	q _{max}	\mathbf{R}^2
Cr (Electroplating)	0.0001	101.5	0.464	0.0004	1250	0.996
Cr (Tannery)	0.0034	496.7	0.8149	0.00062	2000	0.999
Ni (Electroplating)	0.0002	2.9721	0.876	0.00012	166.6	0.8883
Cu (Synthetic)	0.0004	101.5	0.3401	0.013	80.6	0.9998

Fourier transform infrared spectrophotometer was used to study the changes in the biomaterial (Sansevieria *trifasciata*) adsorption. on metal Characteristic vibrational frequencies were observed for various functional groups present on the surface of the biosorbent i.e. an intense broad band was observed at 3417 cm⁻¹ that was ascribed to the -OH stretching vibration of cellulose present in the biosorbent, a broad band found at 2358.3 cm⁻¹ may be due to stretching vibrations of $C \equiv C$ or N=C groups. Similarly, sharp bands at 1654.5 cm⁻¹, and 1459 cm⁻¹ were associated with C=O and C=C groups and the vibrational frequencies in the region 1350 - 1050 cm⁻¹ represent the presence of C-O stretching of alcohol, phenol, ethers and carboxylic acid. After metal biosorption, the bands for C=C, C=O, C=C, N =C, C-O, and O-H, were shifted to 1344-1050 cm⁻¹, 1457 cm⁻¹, 2340.4 cm⁻¹, 1648 cm⁻¹, and 3409 cm⁻¹, respectively that confirmed the metal binding with different functional groups

present on the surface of biomaterial, particularly COO⁻ and OH⁻ groups.

8. Desorption studies

Reusability of the biosorbent is critically important for industrial application. On desorption with 0.5 M HCl and subsequent washing with distilled water, 82, 64, 78.2, 75, % recovery of biosorbent was obtained for Cu Ni and Cr, present in wastewaters.

9. Comparison of biosorption potential of *Sansevieria trifasciata* with other biosorbents

Table 3 furnishes a comparison of q_{max} values (biosorption potential) of S. trifasciata for the removal of Ni. Cu and Cr ions with Langmuir isotherm model based q_{max} values of other biomaterials cited in previous literature. Sansevieria trifasciata was proved to be a better biosorbent for the removal of all the three selected metals than most of the other previously described biosorbents. It exhibited uptakes of 57, 147, 178, and 277 mg g^{-1} for synthetic Cu, Ni (electroplating effluent) and Cr (electroplating, tannery effluents).

Metal	Biosorbent	q _{max}	pН	Reference
	M.olifera bark	30.38	6	[29]
Ni	Modified coir pith	38.9	3.92	[30]
	Barly straw untreated	35.8	4.85	[31]
	Coir pith Carbon	62.5	5	[32]
	Doum seed carbon	3.24-13.51	7	[33]
	Eriobotrya japonica	24.77	6	[34]
	Sansevieria trifasciata	147	6	present study
	Cicer arientum	27.97	5	[35]
Cu	Papaya wood	19.99	5	[36]
	Olive pomace	4.3	5	[37]
	Residual biomas	50.6	4	[38]
	Franxins tree leaf	33.1	5	[39]
	Ulmus tree leaf	69.5	5	[39]
	Rice straw	74.70	7	[40]
	Lawsonia Inermis Plant Leaf			
	Biomass	6.06	5	[41]
	Sansevieria trifasciata	57	4.5	present study
Cr	Activated Carbon	57.7	7	[42]
	Sawdust	39.7	7	[43]
	Tamarindus seed	11.08	7	[44]
	Tur dal husk	96.05	2	[45]
	Trichoderma gamsii Biomass	44.8	-	[46]
	Walnut shell powder	138.89	2	[47]
	Potato peels	3.28	2.5	[48]
	Sansevieria trifasciata	227	6	present study
	Sansevieria trifasciata	178	4	present study

Table 3. Biosorption potential of Sansevieria trifasciata Vs. other biosorbents.

Conclusions:

The results of the study proved that Sansevieria trifasciata biomass as an efficient biosorbent for the removal of Cr (total), Ni (II) and Cu (II) from aqueous solutions or industrial effluents. In only twenty minutes, the biosorption equilibrium was attained for Ni removal from the electroplating industry effluent. Under optimum analytical conditions, this cheaper biosorbent entailed removal efficiencies of as high as 92.7 %. For different effluents, the optimum pH was found to range between 4 and 6 for the removal of the three selected metals. The data obtained for Cr removal was good fitted to Langmuir model while the adsorption phenomenon of Ni and Cu was better described by Freundlich isotherm. Pseudo second order model best described the kinetics of the biosorption process. The hydroxyl and carboxyl function groups were evidenced to be present on the surface of biomaterial by FTIR analysis. These groups were mainly responsible for the removal by this biomass. The results of the study also showed that about 84% of the metals taken up by the biomaterial could be desorbed and reused.

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كفاءة نبات Sansevieria trifasciata في الامتصاص الحيوي لمعالجة التلوث بالمخلفات الصناعية المعدنية السائلة

سعدية راشد طارق فرح إقبال يسرا صفا

قسم الكيمياء، جامعة لاهور للبنات، لاهور، باكستان.

الخلاصة:

درس نبات Sansevieria trifasciata كعامل از الة لمركب الكروم، النحاس، النيكل، في عملية الطلاء الكهربائي والفضلات السائلة للدباغة وقد تم استعمال معاملات مختلفة تؤثر في عملية الامتصاص مثل pH ووقت التماس، وكمية الامتصاص الامثل من خلال استعمال حجم 80 مل من جزيئات الامتصاص الحيوي لتصل الاز الة إلى 91.3% نيكل و 92.7% نحاس عند pH بين 6 و 4.5 على التوالي، في حين تمت إز الة الكروم بصورة مثالية بنسبة 91.34% بالكهرباء و6.94% من مدبغة النفايات السائلة في درجة الحموضة 6.0 و 4.0 على التوالي. وتم العثور على نموذج الدرجة الثانية الز ائفة الافضل لتناسب البيانات الحركية لجميع المعادن كما يتضح من معامل R الأكبر.

وصف تحليل FTIR الامتصاص الحيوي حيث اظهرت وجود الكربوكسيل ومجموعات الهيدروكسيل على سطحه التي كانت مسؤولة عن امتصاص المعادن. وكان أفضل تفسير لبيانات إزالة الكروم من كل من النفايات السائلة هي نموذج Langmuir في حين كانت نتائج إزالة الكروم و النحاس هي الافضل تجهيزاً Freundlich isotlherm. فضلا عن الى ذلك، تمت اعادة 84٪ من الامتصاص الحيوي الى الامتزاز.

الكلمات المفتاحية: الامتصاص الحيوي، المخلفات الصناعية، Freundlich isotherm، Langmuir isotherm ، نبات Langmuir trifasciata.