INTRODUCTION

Heavy metal discharge into water bodies has been increased since last few decades as a result of industrial activities and technological development, which is a serious threat to ecosystem as well as a major health concern due to its persistent nature and accumulation in the food web. Heavy metals are known to be very toxic even in very small concentrations such as exaggerate in respiratory system (carcinogenic), enzymes inhibition, kidney and liver damage as well as physiological and neurological effects. Thus, the removal of heavy metals from wastewater has become mandatory. Various methods have been used for heavy metal removal, including chemical precipitation, neutralization, membrane filtration and adsorption. Among these techniques, biosorption by using agricultural waste has gained considerable attention because of its high efficiency, low cost, more availability and ease of handling.

Chromium is naturally occurring element found in soils, plants and volcanic dust. It is an essential dietary element in low doses and is required to potentiate insulin for normal glucose metabolism. However, its elevated concentrations in the environment are extremely toxic to ecosystem. Chromium is released into the environment from a variety of industrial sources like textile, leather tanning, electroplating and metal finishing industries. Current technologies to remove chromium such as precipitation and ion exchange with synthetic resins are expensive and generate toxic sludge which requires further disposal problems. As a result of these shortcomings, the foregoing concerns have led to an interest in the development of new technologies which can reduce chromium concentrations in environment to acceptable levels at affordable cost.

Biosorption utilizes biological materials as adsorbents and this method has been studied by several researchers as an alternative technique to conventional methods for the heavy metal removal from wastewater. The use of non-living biomaterial containing metal-binding compounds would have the advantage of not requiring utmost care and maintenance as well as being useful in remediating areas with high levels of the heavy metal contaminants.

Rose (Rosa damascena) belongs to family rosaceae. The genus Rosa contains more than 1400 cultivars and 150 species. The flowers of Rosa damascena are used for the production of essential oil and rose water by steam distillation process. Large quantity of rose petals is being used for this purpose in Pakistan as well as in various other parts of the world. The residue of petals left after oil extraction is a waste material and disposed off. In this regard, present study was planned to evaluate the biosorption behaviour of Rosa damascena phytomass (non-useful waste material) towards Cr(III) and Cr(VI) from aqueous solutions. Other then kinetic study, the sorption
conditions such as biosorbent size, pH, temperature, dose and metal initial concentration were optimized to remove the maximum Cr contents from aqueous solution. The biomass pretreatment effect on Cr biosorption was also studied.

**EXPERIMENTAL**

All the chemicals used were of analytical reagent grade, including Cr(SO$_4$)$_3$, K$_2$Cr$_2$O$_7$, concentrated HCl, concentrated H$_2$SO$_4$, NaOH (Merck) and Cr(III) and Cr(VI) atomic absorption spectrometry standard solution (1000 mg L$^{-1}$) (Fluka chemicals).

Sample collection and preparation: The Rosa damascena waste petal biomass was collected from Rose Lab, Institute of Horticulture Sciences, University of Agriculture, Faisalabad, Pakistan. The biomass was first dried in sun light followed by oven dried at 50 ºC for 72 h. The dried biomass sieved through Octagon siever (OCT-DIGITAL 4527-01) for the removal of uneven particle and to obtain adsorbent with a uniform and known particle size. The fraction with 0.25 mm diameter was selected and used for sorption. The sieved material was stored in an airtight plastic bag.

Biomass pretreatment: The grinded biosorbent (0.1 g) of 0.25 mm particle size was treated with 0.1 N HNO$_3$, H$_2$SO$_4$, HCl, NaOH, CaCl$_2$, Na-alginate, PEI-glutaraldehyde and 1 % solution of Moringa olefera seed powder followed by shaking (120 rpm) at 30 ºC for 24 h. Physical treatments involved heating 60 ºC and boiling for 0.5 h while untreated biosorbent was taken as control.

Chromium analysis: The Cr(III) and Cr(VI) concentration were determined using A analyst 30, Perkin Elmer equipped with chromium hollow cathode lamp and acetylene air source at 218 nm wavelength. Calibration for Cr(III) and Cr(VI) was carried by using standard of concentration 1-5 mg L$^{-1}$. The amount of chromium adsorbed was calculated by the simple concentration difference method. The initial concentration of chromium (C$_i$ mg L$^{-1}$), concentration at any time (C$_e$ mg L$^{-1}$) and adsorption capacity (q) was calculated as described$^{11}$. 

\[ q = \frac{(C_i - C_e) \times V}{1000 \times w} \]

Statistical analysis: All experiments were run in triplicate and the arithmetic mean of the results was used in data analysis. All statistical analysis was done using Microsoft Excel 2004, version Office Xp (Microsoft Corporation, USA).

**RESULTS AND DISCUSSION**

Effect of pH: The effect of pH on Cr removal was determined at pre-optimized conditions (30 ºC, 120 rpm, 100 mg L$^{-1}$ of initial Cr concentration and 0.1 g of biosorbent dose of 0.25 mm particle size respectively). The Cr removal efficiency was found pH dependent and responses of Cr(III) and Cr(VI) uptake is shown in Fig. 1. The absorption capacity of Rosa damascena phytomass was found different for Cr(III) and Cr(VI). The Cr(III) absorption was increased constantly up to pH 5. This behaviour of Rosa damascena phytomass for Cr(VI) and Cr(III) might be attributed to different surface chargers by varying pH. So, there was maximum adsorption capacity (q) of 81.35 mg/g for Cr(III) and 86.81 mg/g for Cr(VI) at pH 5 and 2, respectively. The results are in accordance with the previous biosorption studies of Pb by Gossypium hirsutum$^1$.

Sorption as a function of dosage: The dependence of Cr(III) and Cr(VI) biosorption on dose was studied by varying the amount of Rosa damascena phytomass from 0.05 to 0.4 g/100 mL, while keeping other parameters (pH, sorbent particle size, initial metal concentration) constant. An increase of the
The maximum adsorption was occurred with 0.250 mm particle size of biosorbent. The maximum adsorption occurred with 0.250 mm particle size of biosorbent. For Cr(III) and Cr(VI), the highest removal was 61.75 mg L\(^{-1}\) and 73.03 mg L\(^{-1}\), respectively. This was most probably due to the increase in the total surface area, which provides more sorption sites for the metals ions. The enhanced removal of sorbate by smaller particle size has also been reported previously\(^\text{13}\) for Pb and Ni using *Gossypium hirsutum* (cotton) and *Cassia fistula* (Golden Shower) biomass, respectively.

**Temperature effect:** The temperature dependence of Cr(III) and Cr(VI) biosorption by *Rosa damascena* phytomass showed a good compliance with the pseudo second order equation, which are reflected by the high coefficient of correlation. The effect of temperature on the removal of Cr(III) and Cr(VI) from aqueous solution by *Rosa damascena* biomass was studied by varying the temperature from 30 to 70 °C. The maximum removal (%) of Cr(III) and Cr(VI) was obtained at 30 °C (Fig. 1). The equilibrium biosorption capacity decreased with increasing temperature and rate constant also showed same trend, because by increasing temperature the attractive forces between biomass surface and metal ions became weakened and the sorption decreased. At high temperature, the thickness of the boundary layer may decreases and tendency decreases to transfer form solution to biomass\(^\text{14}\).

**Effect of initial metal concentration:** The rate of Cr biosorption on *Rosa damascena* phytomass was also evaluated as a function of Cr initial concentrations. Fig. 1 showed the effect of different initial Cr(III) and Cr(VI) concentrations on their sorption using *Rosa damascena* phytomass. By increasing the initial (25-800 mg L\(^{-1}\)) Cr concentration resulted in greater biosorption until 100 mg L\(^{-1}\) and then there was decreasing trend up to 800 mg L\(^{-1}\). Similar results regarding the initial metal concentration effect on adsorption has also been reported in previous studies\(^\text{14-16}\). The Langmuir and Freundlich adsorption isotherms were used to model the biosorption studies based on metal concentration as precisely described by Hanif et al\(^\text{14}\).

\[
\frac{C_e}{q_m} = \frac{1}{X_m K_l} + \frac{C_e}{X_m}
\]

where, \(q_m\) is the metal ion sorbed (mg/g), \(C_e\) the equilibrium concentration of metal ion solution and \(X_m\) and \(K_l\) are the Langmuir constants. The Freundlich equation is an empirical relationship describing the adsorption of the solutes from a liquid to solid surface. Linearized form of Freundlich equation is:

\[
\log q_m = \frac{1}{n} \log C_e + \log K
\]

where, \(q_m\) is the metal ion sorbed (mg/g), \(C_e\) the equilibrium concentration of metal ion solution (mg/L) and \(K\) and \(1/n\) are constants. Data fitted with Langmuir and Freundlich isotherm models is given in Fig. 2. The \(R^2\) and \(q_{\text{max}}\) values suggested that the Langmuir isotherm describes the sorption process well as compared to model of Freundlich\(^\text{1}\) (Table-1).

\[
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
\text{Metal ion} & \text{Exp. value} & \text{LIP} & \text{FIP} \\
\hline
\text{Cr (III)} & 91.56 & 65 & 0.0985 & 0.9748 & 22.89 & 12.56 & 0.75 & 0.7214 \\
\text{Cr (IV)} & 79.89 & 76 & 0.0421 & 0.9968 & 57.26 & 11.37 & 0.8 & 0.9125 \\
\hline
\end{array}
\]

LIP = Langmuir isotherm parameters and FIP = Freundlich isotherm parameters

![Image](image-url)
Effect of biomass pretreatment: The effect of biosorbent pretreatment on Cr removal efficiency was investigated and results were presented in Fig. 3. According to Yan and Viraraghavan, the biosorbent pretreatment may affect the adsorption capacity of biomass. In this regard, the Rosa damascena phytomass was subjected to different pretreatments agents such as 0.1N HCl, CaCl$_2$, Al(OH)$_3$, HNO$_3$, Na-alginate, H$_2$SO$_4$, NaOH, PEI + glutaraldehyde and 1% Moringa oleifera solution (chemical pretreatments). The sorption capacities (mg g$^{-1}$) of Rosa damascena waste biomass pretreated with mineral acids were in the following order: HNO$_3$ (72.59) > HCl (59.27) > H$_2$SO$_4$ (81.23) > NaOH (67.77), respectively. The sorption capacities (mg g$^{-1}$) of Rosa damascena waste biomass pretreated with chemical pretreatments were in the following order: Heated (72.48) > Al(OH)$_3$ (74.01) > NaOH (64.22) > native (78.12) > boiled (63.48) > native (72.59) > MOSP > PEI + glutaraldehyde. The biosorbent treatment with Na-alginate showed the sorption capacities in the following order: native (78.12) > NaOH (67.77),  respectively. Loaec et al. has also reported the enhanced removal capacity of Cr when biomass was treated with alkali. In case of Na-alginate the sorption capacity was found higher for Cr(III) versus native and was opposite for Cr(VI). The alginates exhibited the best biosorption of metal. Similar results have also been reported by Tsui et al. and Veglio et al. The phytomass pretreated with Moringa oleifera powder showed the sorption capacities (mg/g) as: native (72.59) > Moringa oleifera (64.22) and Moringa oleifera (91.43) > native (78.12) for Cr(III) and Cr(VI), respectively. The biosorbent treatment with Moringa oleifera reduced Cr (III) biosorption capacity because Moringa oleifera is a natural coagulant, contains polyelectrolytes (responsible of coagulation) and organic compounds (can adsorb biomass on surface). The Rosa damascena phytomass pretreated with CaCl$_2$ and PEI + glutaraldehyde showed the sorption capacities in the following order for Cr(III) and Cr(VI), native (72.59) > PEI + glutaraldehyde (61.18) > CaCl$_2$ (48.22) and native (78.12) > PEI + glutaraldehyde (72.48) > CaCl$_2$ (54.38) (mg/g), respectively. PEI pretreatment reduced the sorption of Cr versus native, which might be due to the presence of amino group. The lack of crosslinking of amino group between the biomass and PEI adsorption sites can decreased resulting in less adsorption and precipitation might reduced the biosorption process in the presence of calcium chloride. Biomass was also subjected to heat and boiling treatments. The sorption capacities of both were found to be lower than native biomass because pretreatment could rupture the biomass cells and unavailability of binding sites for Cr attachment. The overall effect of biosorbent pretreatment was found in following order for Cr(III) SA > HNO$_3$ > Al(OH)$_3$ > native > boiled > MOSP > P-G > H$_2$SO$_4$ > NaOH > CaCl$_2$ > HCl > heated, while it was Al(OH)$_3$ > Boiled > CaCl$_2$ > H$_2$SO$_4$ > HCl > Heated > HNO$_3$ > MOSP > NaOH > Native > P-G > SA for Cr(VI).

Effect of kinetics on metal binding: Kinetics of adsorption by any biological material was tested by the pseudo first order expression given by Lagergren and pseudo second order approach.

![Fig. 3. Effect of pre-treatment on Cr(III) and Cr(VI) removal by Rosa damascena waste phytomass](image)

### Table 2: Effect of Kinetics on Cr(II) and Cr(VI) Biosorption by R. damascena Phytomass

<table>
<thead>
<tr>
<th>Metal</th>
<th>Time (min)</th>
<th>Cr (mg L$^{-1}$)</th>
<th>Ce (mg L$^{-1}$)</th>
<th>Q (mg g$^{-1}$)</th>
<th>Removal (%)</th>
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<tr>
<td>Cr(III)</td>
<td>15</td>
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<td>76.54</td>
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<td></td>
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<td>Cr(VI)</td>
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</table>

The first order Lagergren equation (eqn. 3):

$$\log (q_e - q_t) = \log q_e - \frac{t}{K_{1,ads}}$$  \hspace{1cm} (3)

The pseudo second order equation (eqn. 4) is given as follows.

$$\frac{t}{q} = \frac{1}{K_{2,ads}q^2_e} = \frac{t}{q_t}$$  \hspace{1cm} (4)

where, $q_e$ is the mass of metal adsorbed at equilibrium (mg g$^{-1}$), $q_t$ is the mass of metal at time t (min), $K_{1,ads}$ is the first order reaction rate constant of adsorption (min$^{-1}$), $K_{2,ads}$ is the pseudo second order rate constant of adsorption (mg g$^{-1}$ min$^{-1}$). A comparison between Lagergren first order and pseudo second order kinetic model is given in Fig. 4. The pseudo second order kinetic model with higher value of regression coefficient ($R^2 = 0.998$ and 0.999 for Cr(III) and Cr(VI), respectively) fitted well to the data. The effect of metal binding by Rosa damascena biomass results are shown in Table-3. The removal efficiency of Cr(III) and Cr(VI) increased with increasing the contact time before equilibrium is reached. Other parameters such as adsorbent dose, pH, shaking and agitation speed and temperature were kept constant. The Cr(III) and Cr(VI) ions uptake were rapid for first 0.5 h followed by slow sorption till equili-
brium was reached. From this sorption behaviour of Cr(III) and Cr(VI) ions by pretreated and untreated biomasses, it was estimated that two-step mechanism took place. The first step, known as a passive transport, happened quite rapidly (0.5 h), while the second passive diffusion step transport acquired much longer time to complete. Adsorption capacity (q_e) at different time intervals, i.e., 15, 30, 60, 120, 240, 480, 860 and 1440 min was analyzed. The kinetic results were in accordance with previous studies for the removal of heavy metal by bacteria and other microorganisms.

**Conclusion**

It was concluded that the maximum absorption of Cr ions from aqueous solutions occurred at pH 2 for Cr(III) and 5 for Cr(VI), 0.250 mm biosorbent particle size and 0.05 g biosorbent dose of *Rosa damascena* phytomass. The biomass pretreatment considerably enhanced the absorption of Cr(III) and Cr(VI) versus untreated phytomass. The Cr(III) and Cr(VI) adsorption on waste *Rosa damascena* phytomass biomass well fitted to the Langmuir adsorption isotherm. The uptake of Cr(III) and Cr(VI) occurred in two phases, a rapid surface adsorption within 0.5 h followed by slow intracellular adsorption until equilibrium was reached. The whole adsorption process was well described by pseudo second order. The negative Gibbs free energy indicated that the Cr absorption on *Rosa damascena* phytomass was spontaneous process and *Rosa damascena* phytomass (Rosa petels biomass wasted after oil extraction) could be used to remove the Cr(III) and Cr(VI) form aqueous solution.

**ACKNOWLEDGEMENTS**

The authors are grateful to Dr. M. Shahid for providing assistance, especially for kinetic study and modeling.

**REFERENCES**


### Table 3

<table>
<thead>
<tr>
<th>Metal</th>
<th>q_e (mg g⁻¹)</th>
<th>kₙ,ads</th>
<th>R²</th>
<th>q_e (mg g⁻¹)</th>
<th>kₙ,ads</th>
<th>R²</th>
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</thead>
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<td>Cr(III)</td>
<td>38.52</td>
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<td>0.9855</td>
<td>76.52</td>
<td>77.52</td>
<td>0.9895</td>
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<tr>
<td>Cr(VI)</td>
<td>57.45</td>
<td>5.75 x 10⁻³</td>
<td>0.9647</td>
<td>88.07</td>
<td>90.9</td>
<td>0.9975</td>
</tr>
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</table>

Fig. 4. Comparison between pseudo first order (a) and pseudo second order (b) for Cr(III) and Cr(VI) biosorption by *Rosa damascena* waste phytomass

**Gibbs free energy (ΔG°):** The Gibbs free energy was also calculated and the results for all treatment were found negative. According to Riaz et al., the negative values of Gibbs free energy indicated that the Cr absorption from aqueous solution was spontaneous in nature on low as well as high concentrations.