Kinetic Study of Cr(III) and Cr(VI) Biosorption Using
Rosa damascena Phytomass: A Rose Waste Biomass

M. Jamshaid Iqbal[1,*], Farhan Cecil[1], Khalil Ahmad[2], Munawar Iqbal[1], M. Mushtaq[1], M.A. Naeem[3] and T.H. Bokhari[4]

[1]Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad-38040, Pakistan
[2]Department of Chemistry, The University of Faisalabad, Faisalabad, Pakistan
[3]Department of Physics, University of Agriculture, Faisalabad-38040, Pakistan
[4]Department of Chemistry, Government College University, Faisalabad, Pakistan

*Corresponding author: E-mail: jimychemist@hotmail.com; mmushtaq_doc@yahoo.com

In present study, Cr(III) and Cr(VI) sorption capacity of *Rosa damascena* phytomass from aqueous solution was evaluated. The *R. damascena* phytomass biosorption revealed that smaller biosorbent size (< 0.4 g), dose (< 0.1 g), pH (2 and 5 for Cr VI and III) and 100 mg L^{-1} initial metal concentration were more suitable for better biosorption from aqueous medium. The Langmuir isotherm model and pseudo second order kinetic model fitted well to the data of Cr(III) and Cr(VI) biosorption. The negative value of Gibbs free energy (ΔG°) indicated the spontaneous absorption process. The *R. damascena* biomass pre-treatment enhanced biosorption considerably and it is concluded that the *R. damascena* biomass (waste material) might be used for biosorption of Cr(III) and Cr(VI) from aqueous solution.

Key Words: *R. damascena* phytomass, Chromium removal, Langmuir isotherm, Absorption kinetic.

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[1-4]. Heavy metals are known to 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[1,5,6].

Chromium is naturally occurring element found in soils, plants and volcanic dust. It is an essential dietary mineral 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[7,8].

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[9,10].

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 worlds. 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 *R. damascena* phytomass (non-useful waste material) towards Cr(III) and Cr(VI) from aqueous solutions. Other then kinetic study, the sorption
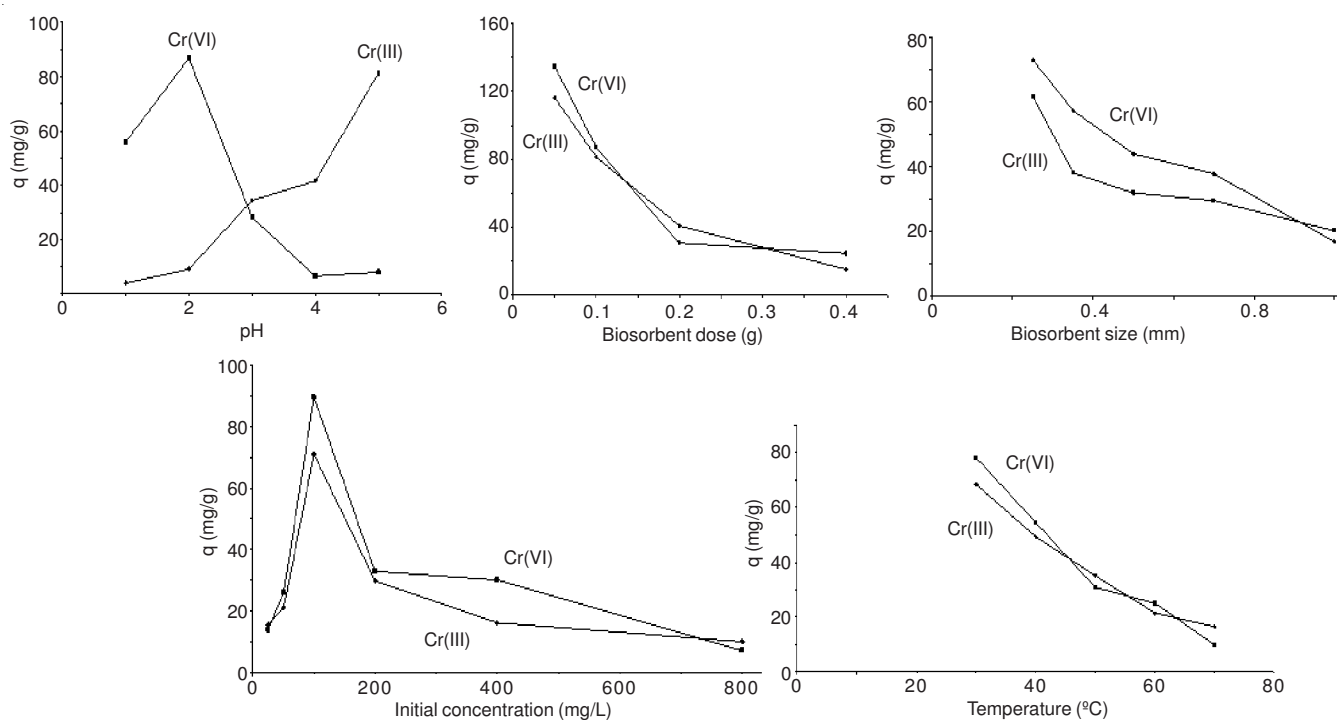
Fig. 1.   Effect of pH, biosorbent dose, biosorbent size, metal initial concentration and temperature on Cr(III) and Cr(VI) biosorption by *Rosa damascena* waste phytomass

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 $Cr_2(SO_4)_3$, $K_2Cr_2O_7$, concentrated HCl, concentrated H_2SO_4, NaOH (Merck) and Cr(III) and Cr(VI) atomic absorption spectrometry standard solution (1000 mg L^{-1}) (Fluka chemicals). The experimental work was carried out in University of Agriculture and University of Faisalabad, Faisalabad, Pakistan

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 though 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_2SO_4, HCl, NaOH, $CaCl_2$, Na-alginate, PEI-gluteraldehyde 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 = (C_i-C_e) V/1000 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 damascene* phytomass was found different for Cr(III) and Cr(VI). The Cr(VI) absorption capacity was found highest at pH 2 and then there was constant decrease until pH 5, while Cr(III) absorption was increased constantly up to pH 5. This behaviour of *Rosa damascene* phytomass for Cr(VI) and Cr(III) might be attributed to different surface chargers by varying pH. So, there was maximum adsorption capacity (q_e) 81.35 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

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS FOR Cr(III) AND Cr(VI) UPTAKE BY *R. damascena* PHYTOMASS

Metal ion	Exp. value	LIP			FIP			
	q_{max} (mg/g)	X_m (q_{max}) (mg/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	K (mg/g)	R^2	1/n
Cr (III)	91.56	65	0.0985	0.9748	22.89	12.56	0.75	0.7214
Cr (IV)	79.89	76	0.0421	0.9968	57.26	11.37	0.8	0.9125
LIP = Langmuir isotherm parameters and FIP = Freundlich isotherm parameters								

amount of *Rosa damascena* phytomass decreased the biosorption capacity (q_e) significantly (P < 0.05). The effect of sorbent dosage on the percentage removal of Cr is shown in Fig. 1. The bisorption capacity of the rose waste biomass found highest at 0.05 g dose and then there was a constant decreasing trend by increasing the biosorbent dose until 0.4 g. This behaviour might be due to the availability of more adsorption sites for lower absorbent concentration and over-lapping or aggregation of adsorption sites with the increase in absorbent dose. Similar result has been reported by Riaz *et al.*[1] for Pb biosorption from aqueous solution using *Gossypium hirsutum*. They also achieved the maximum adsorption with low biomass concentration and sorption capacity declined smoothly by increasing biomass dose.

Influence of biosorbent size: The influence of biosorbent size on Cr biosorption was evaluated at 30 ºC, 0.1 g dose and 120 rpm. The pH of Cr(III) and Cr(VI) solution was 5 and 2 (pre-optimized), respectively. The results obtained for biosorbent particle size (0.250, 0.335, 0.500, 0.710 and 1 mm) for adsorption capacities (q_e) of Cr(III) and Cr(VI) on *Rosa damascena* phytomass are shown in Fig. 1. Results showed that there was more dominant removal of Cr(III) and Cr(VI) ions by the smaller size of biosorbent particles. The maximum adsorption was 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[12] 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 ºC. The maximum removal (%) of Cr(III) and Cr(VI) was obtained at 30 ºC (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[13].

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[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.*[14].

$$C_e/q_e = 1/X_m K_L + C_e/X_m \qquad (1)$$

where, q_e 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:

$$\log q_e = 1/n \log C_e + \log K \qquad (2)$$

where, q_e 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_{max} values suggested that the Langmuir isotherm describes the sorption process well as compared to model of Freundlich[1] (Table-1).
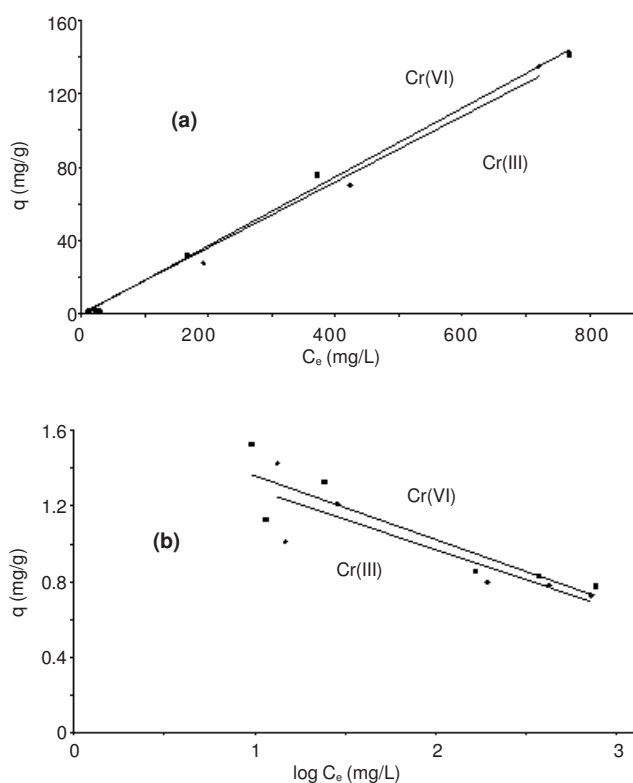

Fig. 2.   Freundlich (a) Langmuir (b) adsorption isotherm for Cr(III) and Cr(VI) biosorption by *Rosa damascena* waste phytomass

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[17], 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, CaCl₂, Al(OH)₃, HNO₃, Na-alginate, H₂SO₄, NaOH, PEI + glutraldehyde and 1 % *Moringa olefera* solution (chemical pretreatments). The sorption capacities (mg g⁻¹) of *Rosa damascena* waste biomass pretreated with mineral acids were in the following order: HNO₃ (74.01) > native (72.59) > H₂SO₄ (59.27) > HCl (41.5) and H₂SO₄ (81.23) > native (78.12) > HNO₃ (61.75) > HCl (49.87), respectively for Cr(III) and Cr(VI). According to Bhatti *et al.*[18] acids can enhance uptake capacity of biomass by increasing the surface area and porosity of biomass. For base pretreatment, the order for Cr(III) and Cr(VI) removal was found as; Al(OH)₃ (73.98) > native (72.59) > NaOH (58.59) and Al(OH)₃ (81.55) > native (78.12) > NaOH (67.77), respectively. Loaec *et al.*[19] 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 ability to remove Cr(III). According to Fourest *et al.*[20] the carboxylate groups of alginates are the main binding sites for metal. Similar results have also been reported by Tsui *et al.* and Veglio *et al.*[21, 22]. The phytomass pretreated with *Moringa olefera* powder showed the sorption capacities (mg/g) as: native (72.59) > *Moringa olefera* (64.22) and *Moringa olefera* (91.43) > native (78.12) for Cr(III) and Cr(VI), respectively. The biosorbent treatment with *Moringa olifera* reduced Cr (III) biosorption capacity because *Moringa olefera* is a natural coagulant, contains polyelectrolytes (responsible of coagulation) and organic compounds (can adsorb biomass on surface). The *Rosa damascena* phytomass pretreated with CaCl₂ and PEI + glutraldehyde showed the sorption capacities in the following order for Cr(III) and Cr(VI), native (72.59) > PEI + glutraldehyde (61.18) > CaCl₂ (48.22) and native (78.12) > PEI + glutraldehyde (72.48) > CaCl₂ (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[23]. The overall effect of biosorbent pretreatment was found in following order for Cr(III) SA > HNO₃ > Al(OH)₃ > native > boiled > MOSP > P-G > H₂SO₄ > NaOH > CaCl₂ > HCl > heated, while it was Al(OH)₃ > Boiled > CaCl₂ > H₂SO₄ > HCl > Heated > HNO₃ > 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[1,14].
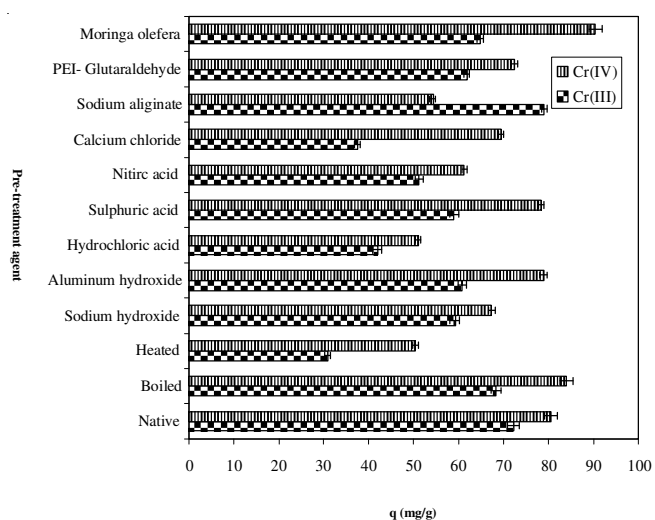

Fig. 3. Effect of pre-treatment on Cr(III) and Cr(VI) removal by *Rosa damascena* waste phytomass

TABLE-2
EFFECT OF KINETICS ON Cr(II) AND Cr(VI) BIOSORPTION
BY *R. damascena* phytomass

Metal	Time (min)	Ci (mg L⁻¹)	Ce (mg L⁻¹)	Ci-Ce (mg L⁻¹)	Q (mg g⁻¹)	Removal (%)
Cr(III)	15	100.29	76.54	23.75	23.75	23.68
	30	98.86	59.38	39.48	39.48	39.94
	60	99.27	52.61	46.66	46.66	47.02
	120	100.58	49.52	51.06	51.06	50.76
	240	99.98	36.36	63.62	63.62	63.63
	480	100.26	36.84	63.42	63.42	63.25
	860	100.89	36.84	64.05	64.05	63.48
	1440	99.74	33.46	66.28	66.28	66.45
Cr(VI)	15	100.21	70.19	30.02	30.02	29.95
	30	100.9	56.54	44.36	44.36	43.96
	60	99.93	52.13	47.8	47.8	47.83
	120	99.58	33.05	66.53	66.53	66.81
	240	98.98	24.23	74.75	74.75	75.52
	480	100.17	25.43	74.74	74.74	74.61
	860	99.53	24.79	74.74	74.74	75.09
	1440	100.02	25.27	74.75	74.75	74.73

The first order Lagergren equation (eqn. 3):

$$\log (q_e-q) = [\log q_e - \{K_{1,adst}/2.303\}] \qquad (3)$$

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

$$t/q = 1/K_{2,ads} \, q_{e2} = t/qt \qquad (4)$$

where, q_e is the mass of metal adsorbed at equilibrium (mg g⁻¹), qt 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 to 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-

TABLE-3
COMPARISON BETWEEN THE PSEUDO FIRST ORDER AND PSEUDO SECOND ORDER
KINETIC MODELS FOR Cr(III) AND Cr(VI) UPTAKE BY *R. damascena* PHYTOMASS

	Pseudo first order kinetic Model			Exp. value	Pseudo second order kinetic model		
Metal	q_e (mg g^{-1})	k_1,ads	R^2	q (mg g^{-1})	q_e (mg g^{-1})	k_2, ads	R^2
Cr(III)	38.52	8.9×10^{-3}	0.9855	76.52	77.52	7.98×10^{-4}	0.9985
Cr(VI)	57.45	5.75×10^{-3}	0.9647	88.07	90.9	3.31×10^{-4}	0.9997

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[14]. 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[3,24].

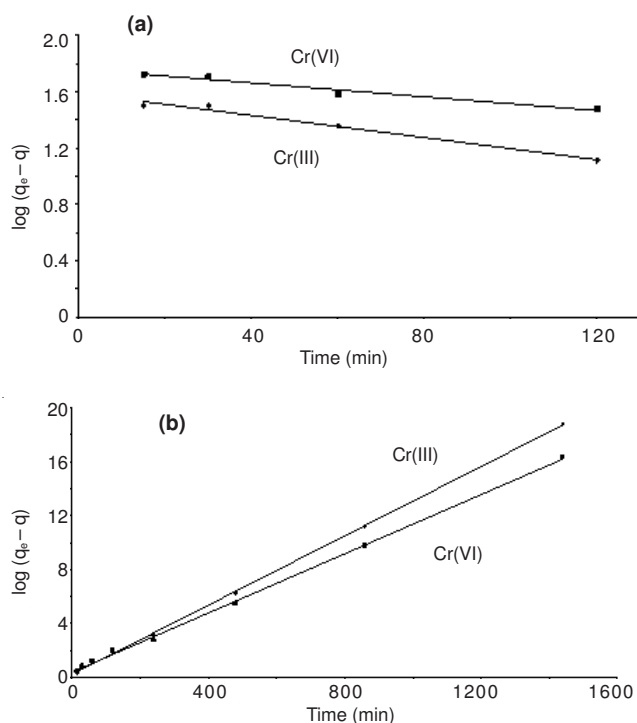

Fig. 4. Comparison between pseudo first order (a) and pseudo second order (b) for Cr(III) and Cr(VI) biosorption by *Rosa damascena* waste phytomass

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.*[1] 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.

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* phytomas. 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* phytomas 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* phytomas was spontaneous process and *Rosa damascena* phytomas (Rosa petels biomass wasted after oil extraction) could be used to remove the Cr(III) and Cr(VI) form aqueous solution.

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