KINETIC AND EQUILIBRIUM STUDIES OF CR(III) AND CR(VI) SORPTION FROM AQUEOUS SOLUTION USING *ROSA GRUSS AN TEPLITZ* (RED ROSE) WASTE BIOMASS

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(Received: November 9, 2007 - Accepted: July 17, 2008)

ABSTRACT

The biosorption of Cr(III) and Cr(VI) from synthetic solution using dried untreated and pretreated *Rosa gruss an teplitz* waste biomass was evaluated in this study. The results showed that initial pH, biosorbent dose, sorbent particle size, initial metal concentration, time and temperature affected chromium uptake capacity of rose biomass. The effect of twenty different pretreatments including gaseous and other reagents on Cr(III) and Cr(VI) uptake capacity of *Rosa gruss an teplitz* waste biomass was comprehensively described. Uptake capacity of *Rosa gruss an teplitz* waste biomass was significantly affected after pretreatment. The metal uptake capacity of biomass was not only found related to nature of pretreatment but also found strongly related to oxidation state of chromium. The estimation of the correlation coefficients for Cr(VI) showed that the experimental data fit better to Freundlich model. The Langmuir isotherm provided the best correlation for Cr(III) onto the rose waste biomass. The biosorption phenomenon was dependent on the temperature with maximum adsorption at 30˚C. Biosorption of Cr(III) and Cr(VI) ions on to biomass followed pseudo 2nd order adsorption kinetic model. The results confirmed that rose waste biomass is a potential biomaterial to remove Cr(III) and Cr(VI) ions with a high biosorption capacity 45.03 mg/g and 48.75 mg/g for Cr(III) and Cr(VI) respectively.

Keywords: biosorption, pretreatment, Cr(III), Cr(VI), biomass.

INTRODUCTION

Contamination of toxic metals in the aquatic environment is a widespread phenomenon, especially in the developing countries where high-cost remediation technology is not affordable [1]. Heavy metals, often present in the industrial waste waters, are hazardous to the aquatic ecosystem and pose possible human health risk. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings, plants and animals [2, 3]. From the eco-toxicological point of view, chromium is one of the contaminants, which exists in hexavalent and trivalent forms. Hexavalent form is more toxic than trivalent and requires more concern. Strong exposure of Cr(VI) causes cancer in digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [4, 5]. Chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile, steel fabrication and canning industries. These industries produce large quantities of toxic waste water effluents. It is therefore, essential to remove chromium from waste water before disposal. Chemical precipitation, oxidation/reduction, mechanical filtration, ion exchange, membrane separation, photocatalytical and carbon adsorption are among the variety of treatment processes widely used for the removal of toxic heavy metals from the waste streams [6, 7]. These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1–100 mg/l.These methods have several disvantages like high cost, incomplete removal, low selectivity and high energy consumption [8]. Others disadvantages are high reagent requirements and generation of toxic sludge which is often difficult to dewater and also requires extreme caution in its disposal [9]. Biosorption is a low-cost technology for removing anthropogenic metals from water, using readily available biomass from nature [1]. Biosorption is a property of certain types of inactive, non-living biomass to bind and concentrate heavy metals from even very dilute aqueous solutions [10].

The major advantages of biosorption include low cost, high efficiency of heavy metal removal from dilute solutions, regeneration of the biosorbent and possibility of metal recovery [11]. Removal of heavy metals from aqueous solution by using inactive and dead biomass is an innovative and alternative technology for heavy metals from aqueous solution and wastewater [12, 13]. Their efficiency depends on the capacity, affinity and specificity including physico-chemical nature. Two types of biological materials can be used: living or dead biomass. Biosorption by dead biomass is often faster, since only passive cell wall based binding transport into the cell occurs. Another advantage of using dead biomass is the easier and nondestructive recovery of the adsorbed metals, which allows regeneration of the biosorbent material [14]. There are some limitations pertaining to the usage of living organisms as sorbent, e.g. they can not function at low pH level of metal ion [15]. Metals accumulated inside the cells of the living biomass, however, can often be recovered only when the cell is destroyed [14]. Rosa is known as queen of flowers and one of the most favorite flowers through out the world. Huge quantities of *Rosa gruss an teplitz* (red rose) are being used for rose water and essential production through steam or hydro-distillation. The biomass left after extraction is a waste material with no commercial importance is selected as biosorbent for present study.

The present study was undertaken with following objectives:

• To investigate the use of red rose waste biomass as a biosorbent for Cr(III) and Cr(VI).

• To study the effect of different experimental conditions such as pH, biosorbent doze, biosorbent size, initial metal concentration, temperature and shaking speed on sorption process.

• To evaluate the effect of pretreatment on Cr adsorption capacity of red rose waste biomass.

MATERIALS AND METHODS

Reagents

All the reagents used in this study were of analytical grade.

***Rosa gruss an teplitz* biomass**

In the present study *Rosa gruss an teplitz* biomass was selected as sorbent for removal of Cr(III) and Cr(VI) from aqueous solution. *Rosa gruss an teplitz* biomass used in this study was obtained from Rose Laboratory, Institute of Horticulture Sciences, University of Agriculture, Faisalabad, Pakistan, sampled, extensively washed with distilled water to remove particulate material from their surface, and oven dried at 60˚C for 72 h. Dried biomass was cut, ground using food processor (Moulinex, France) and then sieved (< 0.250-1.00 mm).

Pretreatment of biomass

The chromium uptake capacity was tested using physical and chemical pretreatments of red rose waste biomass. Biomass was physically modified using heating (5g of biomass heated up to 60 ˚C for 30 min in electrical oven), boiling (5g of biomass was taken in 100 ml of deionized distilled water (DDW), boiled for 30 min and filtered through filter paper (Whatman No, 40 ashless). For chemical pretreatment biomass was pretreated with 0.1N NaOH, 0.1N $Al(OH)_3$, 0.1N HCl, 0.1N H_2SO_4, 0.1N HNO_3, conc. $(NH_4)_2SO_4$ conc. $CaCl_2$, acetone, 0.1N CH_3OH, 0.1N EtOH, 0.1N C_6H_6, 0.1N formaldehyde, 1% EDTA, 1% potash alum, 1% *Moringa Olifera* powder, 1% Triton-X-100, (5 g of biomass/ 100 ml of each chemical solution), 1% κ-carrageenen, 1% alginic acid sodium salt, 1% alginic acid calcium salt, 1% glutaraldehyde, 1% polyethyleneimine solution (5g of biomass/ 50 ml of each chemical solution) polyethyleneimine + glutaraldehyde (50 mL of each solution + 5 g of biomass) in orbital shaking incubator (PA 250/25. H) at 150 rpm and 30˚C for 15 min. The biomass was also pretreated with CO_2 and H_2S gas. Each gas was passed through 5g of biomass soaked in 100 mL of DDW at the rate of 10 ml/min for 10 min. These pretreatments were done to analyze enhancement or decrease in adsorption capacity of biomass [16, 17, 18]. Then the pretreated biomasses were filtered through (Whatman No. 40, ashless) and washed extensively with deionized distilled water up to neutral pH, followed by drying and grinding.

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Digestion of biomass

Rosa gruss an teplitz waste biomass was wet digested by taking 1 g of biosorbent in 20 mL of conc. HNO_3 followed by heating at 60°C for 15 min. Then 5 ml of H_2O_2 were added and then whole mixture was heated at 100°C for 10 min. After cooling, sample is diluted up to 50 ml using DDW. The sample was then analyzed for Cr, Co, Cu, Mn, Pb, Fe, Mg, Na, Zn, K and Li using Perkin-Elmer AAnalyst 300 Flame Atomic Absorption Spectrometer (FAAS) and Flame Photometer.

Cr(III) and Cr(VI) solutions

Stock Cr(III) and Cr(VI) solutions (1000 mg/L) were prepared by dissolving 3.769 g of $Cr_2(SO_4)_3$ and 2.826 g of $K_2Cr_2O_7$ in 100 mL of deionized distilled water (DDW) and diluting quantitatively to 1000 mL using DDW Cr(III) and Cr(VI) solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW. Glassware and polypropylene flasks used were overnight immersed in 10 % (v/v) HNO_3 and rinsed several times with DDW.

Batch biosorption studies

The influence of different experimental parameters such as pH 1-5 for Cr(III) and 1-10 for Cr(VI), sorbent dose (0.05, 0.1, 0.2, 0.3 and 0.4 g), sorbent size (< 0.250, 0.250-0.350, 0.350-0.500, 0.500-0.710 and 0.710-1.00 mm) , initial metal concentration (25, 50, 100 and 200 mg/l for Cr(III) and 25, 50, 100, 200, 400 and 800 mg/l for Cr(VI), temperature (40, 50, 60 and 70°C), shaking speed (0, 50, 100 and 150 rpm) and contact time (15 to 1440 min) on sorption process was evaluated during study. For adjusting the pH of the medium 0.1N solutions of NaOH and HCl were used. The flasks were placed on a rotating shaker (PA 250/25.H) with constant shaking. At the end of the experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman No. 40, ashless).

Determination of the Cr(III) and Cr(VI) contents in the solutions

The concentration of Cr(III) and Cr(VI) in the solutions before and after the equilibrium was determined by flame atomic absorption spectrometry (FAAS), using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer equipped with an air–acetylene burner and controlled by Intel personal computer. The analytical wavelength was set at 218 nm. The instrument was periodically checked with known standard throughout the analysis. The detection limit was 0.005 mg/l.

Metal uptake

The Cr(III) and Cr(VI) uptake was calculated by the simple concentration difference method (Eq.1).

$$q_e = (C_i - C_e)V/1000w \qquad (1)$$

where V is the volume of the solution in mL, w the mass of the sorbent in g, C_i (mg/l) initial concentration, C_e (mg/l) equilibrium concentration and q_e (mg/g) metal uptake capacity.

Statistical analysis

All the experiments were done in triplicate and the data were reported as mean ±SD (standard deviation) values.

RESULT AND DISCUSSIONS

The studies were carried out with untreated and treated biosorbent. The effect of different process variables such as pH, temperature, time etc., on the untreated biosorbent are described below:

Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the of the adsorbate during reaction. At pH value 1, the dominant species of Cr ions in solution are CrO_4^{2-} and $Cr_2O_7^{2-}$ i.e., Cr(VI) [19]. These anions would be expected to interact more strongly with the ligands carrying positive charges. The maximum biosorption of Cr(III) was observed at pH 5.0 with untreated biosorbent (Fig. 1). When pH was further increased up to 6.0, the percentage adsorption is decreased. Because OH^- ions increased the hindrance of diffusion as well as some of the divalent cations may react with OH^- ion and precipitated and there by decreased the free metal ions available in the solution [20]. At lower pH, there may be competition between H^+ and Cr(III) ions and thus decreased the adsorption capacity of biomass for the metal ion. These results are in close agreement of Zubair *et al*. [21], who reported that maximum uptake of Cr(III) and Cr(VI) by *Citrus reticulata* biomass was observed at pH 5 and 2 respectively.

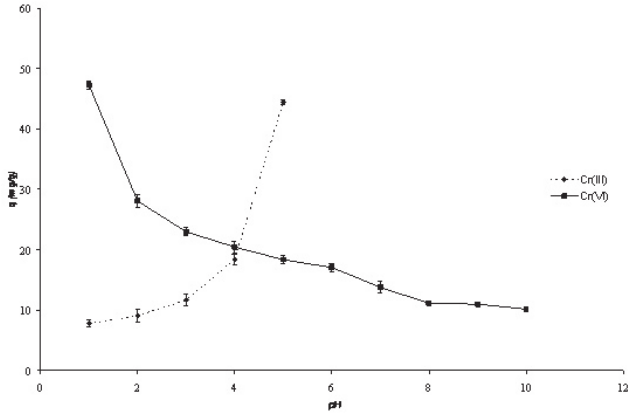

Figure 1: Effect of pH on the uptake of Cr(III) and Cr(VI) from the aqueous solution using *Rosa gruss an teplitz* (red rose) waste biomass.

The highest Cr(VI) removal by rose biomass was observed at p H 1.0, and removal efficiency decreased with an increase in pH. At low pH values, the surface of the sorbent would also be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the biosorbent by greater attractive forces. Hence, biosorption increases with an increase in the acidity of the solution. But as the pH rises, the concentration of OH^- ions increases and overall charge on the biomass surface becomes negative. This causes a hindrance to the biosorption of negatively charged chromium ions such as $Cr_2O_7^{2-}$, CrO_4^{2-} resulting in a decrease of biosorption of chromium at higher pH levels. Niu and Volesky, Tewari *et al.* Bishnoi *et al.* [22, 23, 24] observed the maximum biosorption of Cr(III) at the pH 5.0 with untreated *spirogyra* spp. Kratochvil *et al.* [25] reported that the optimum pH for the efficient removal of total chromium by the seaweed *Sargassum* biomass was approximately between 2.0 and 2.5. Maximum Cr(VI) biosorption onto chitin was observed in the pH range of 2.0-3.0 [26]. Although pH values around 1.0-2.0 have been also used [21, 23].

Effect of temperature

The biosorption capacity for chromium decreased with an increase in temperature, although it did not show a consistent pattern. This could be attributed to the possible damage to active sites in the biomass at higher temperatures [27]. The results indicated that the maximum biosorption (44.44 and 48.75 mg/g) of Cr(III) and Cr(VI) occurred at 30°C and then decreases gradually.

The maximum sorption capacities at various temperatures did not take into account the possible interference effect from other ions in the solution [27]. A decrease in the equilibrium biosorption capacity of Pb(II), Ni(II), and Cr(VI) by *S. cerevisiae* in the temperature interval of 25-40 °C was reported by Ozer and Ozer [28].

Effect of biosorbent dose

The dependence of Cr(III) and Cr(VI) sorption on dose was studied by varying the amount of adsorbents while keeping other parameters (pH, agitation speed, and contact time) constant. The results showed that removal efficiency of the adsorbent generally improved with increasing dose. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. The maximum adsorption of Cr(III) was achieved with biomass concentration 0.05 g and of Cr(VI) with 0.1 g of biosorbent. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent [29]. The results can be explained as a consequence of a partial aggregation, which occurs at high biomass concentration giving rise a decrease of active sites [30-33]

Effect of shaking speed

The effect of agitation speed on removal efficiency of Cr(III) and Cr(VI) was studied by varying the speed of agitation from 0 (without shaking) to 150 rpm, while keeping the optimum dose of adsorbent and optimum pH constant. It was generally observed that the Cr(III) and Cr(VI) ions removal generally increased with increasing agitation speed. The Cr removal efficiency increased when agitation speed increased from 50 rpm to 100 rpm. These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of Cr(III) and Cr(VI) ions towards the surface of the adsorbents Nomanbhay and Palanisamy [29], but this is true up to a certain limit.

Effect of particle size

The effect of altering particle size on the Cr(III) and Cr(VI) ions uptake by red rose waste biomass showed that there was a more dominate removal of metal ions by smaller particles. The maximum adsorption occurred with 0.250 mm biosorbent size. This was most probably due to increase in the total surface area which provided more sorption sites for metal ions [34].

Effect of time

The experiments were conducted to determine the time required for red rose biomass to bind the Cr(III) and Cr(VI) ions. Results (Fig. 2) indicated that removal efficiency increased with an increase in contact time before equilibrium is reached. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system. It can be seen that Cr removal efficiency increased when contact time was increased from 15 to 240 min. Adsorption got slow down in later stages because initially a large number of vacant surface sites may be available for adsorption and after some time, the remaining vacant surface sites may be difficult to occupy due to forces between the solute molecules of the solid and bulk phase [35-37]. The diminishing removal with increasing time may also be due to intraparticle diffusion process dominating over adsorption [1,38].

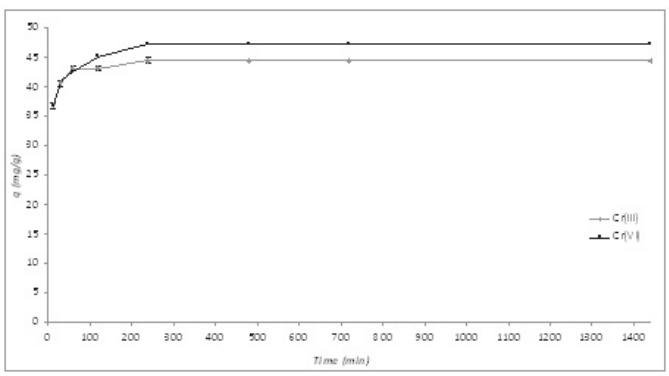

Figure 2: Effect of contact time on the sorption of Cr(III) and Cr(VI) at pH 5.0 and 1.0 using *rosa gruss an teplitz* (red rose) waste biomass.

Kinetic study

The sorption data of Cr(III) and Cr(VI) uptake by *Rosa gruss an teplitz* biomass fitted with pseudo-first-order and pseudo-second-order kinetic models are shown in Figures 6a and 6b.

The linearlized form of first order Lagergren equation is given as (Eq. 1) (Fig. 3).

$$log(q_e - q) = log\ q_e - \frac{k_{1,ads}\, t}{2.303} \qquad (1)$$

The pseudo second order equation (Eq. 2) is (Fig. 4):

$$\frac{t}{q} = \frac{1}{k_{2,ads}\, q_e^{\,2}} + \frac{t}{q_t} \qquad (2)$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t (min.), $k_{1,ads}$ the first order reaction rate of adsorption (per min.), $k_{2,ads}$ the pseudo second order rate constant of adsorption mg/g min^{-1}

The results showed that coefficient of correlation (R^2) for the pseudo-second-order kinetic model is much higher in comparison to pseudo-first-order model. The other fact that is observed, the close agreement between the estimated q_e (mg/g) values and experimental q_e (mg/g) values. Both these observations suggested that the Cr(III) and Cr(VI) sorption by *Rosa gruss an teplitz* biomass followed well the pseudo-second-order kinetic model, which relies on the assumption that biosorption may be the rate limiting step [34].

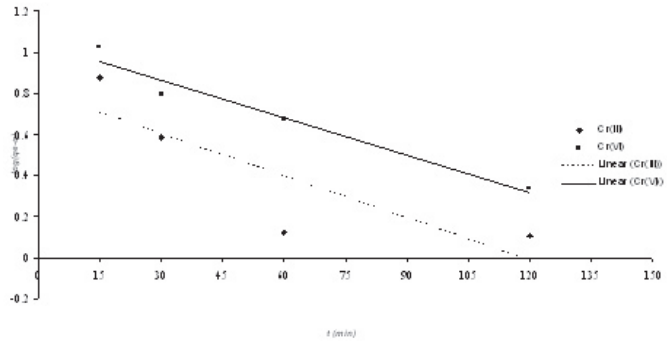

Figure 3: Lagregren pseudo first order kinetic model for biosorption of Cr(III) and Cr(VI) by *Rosa gruss an teplitz* (red rose) waste biomass.

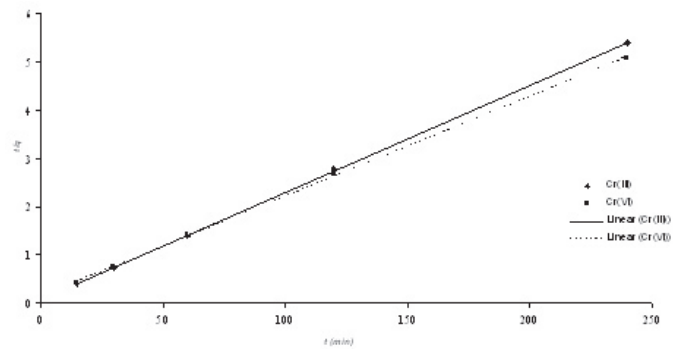

Figure 4: Pseudo 2nd order kinetic model for biosorption of Cr(III) and Cr(VI) by *Rosa gruss an teplitz* (red rose) waste biomass.

Initial metal concentration

The rate of adsorption is a function of initial concentration of metal ions, which makes it an important factor to be considered for effective biosorption [34, 39]. The initial concentration of Cr(III) was varied from 25 to 200 mg/l and of Cr(VI) varied from 25 to 800 mg/l at temperature 30°C, dose 0.1g and sorbent size 0.250 mm. The uptake of Cr(III) and Cr(VI) increased with increase in initial metal concentration (Figure 5).

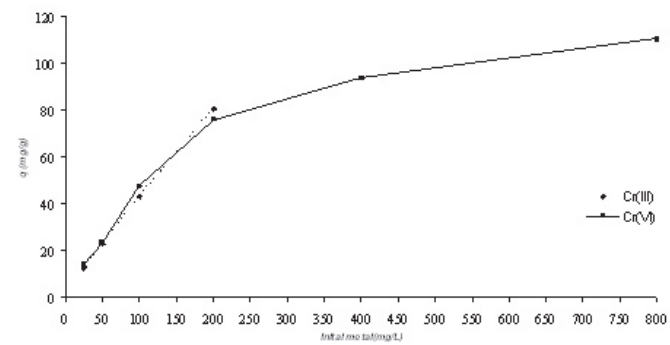

Figure 5: Effect of initial metal concentration on the sorption of Cr(III) and Cr(VI) by *Rosa gruss an teplitz* (red rose) waste biomasss.

The sorption characteristic represented that surface saturation was dependent on the initial metal ion concentrations. At low concentrations adsorption sites took up the available metal more quickly. However, at higher concentration, metal ions need to diffuse to biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at slower rate [34]. The chemistry of adsorption is relatively complicated. Modeling of equilibrium data was done using most widely used Langmuir and Freundlich isotherm models. In the Langmuir model, maximum monolayer adsorption capacity, q_{max}

(mg/g) and other parameters were determined from following linearlized form of equation (Eq. 3):

$$C_e/q_e = 1/q_{maxKL} + C_e/q_{max} \qquad (3)$$

where q_e is the metal ion sorbed (mg/g), Ce the equilibrium concentration of metal ions solution and K_L is the Langmuir adsorption constant. The heterogeneous adsorption capacity, q_e (mg/g) of red rose waste biomass for Cr(III) and Cr(VI) was determined by following log form of Freundlich isotherm (Eq. 4):

$$log\ q_e = 1/n\ log\ C_e + log\ k \qquad (4)$$

The linearlized regression plots of Langmuir and Freundlich isotherms for Cr(III) and Cr(VI) uptake by red rose waste biomass are presented in Figures 6 and 7 respectively. The magnitude of experimental q_{max} for rose waste biomass was 80.22 and 110.24 mg/g for Cr(III) and Cr(VI), respectively. A comparison between Langmuir and Freundlich isotherm models is tabulated in Table 1.

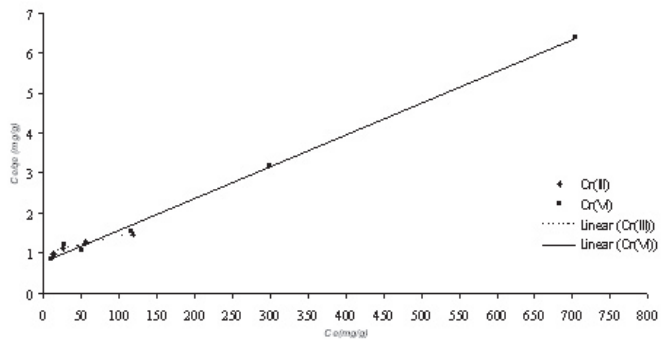

Figure 6: Linearlized Langmuir isotherm models for the sorption of Cr(III) and Cr(VI) by *Rosa gruss an teplitz* (red rose) waste biomass.

Table 1: Comparison of Langmuir and Freundlich isotherm parameters for Cr(III) and Cr(VI) uptake by *Rosa gruss an teplitz* (red rose) waste biomass.

Metal	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	q_{max} (mg/g)	K_L (L/mg)	R^2	q_{max} (mg/g)	q_{max} (mg/g)	K (mg/g)	1/n	R^2
Cr(III)	232.55	4.33×10^{-3}	0.923	80.22	79.95	8.77	0.82	0.999
Cr(VI)	125	1.05×10^{-2}	0.996	110.24	141.82	4.75	0.51	0.914

The Freundlich constant (K), q_{max} and R^2 for Cr(III) determined from model indicated that this model better described the adsorption process in comparison to Langmuir model. This suggested that Cr(III) ions adsorbed on to the surface in a multilayer pattern. The magnitude of n, R^2 and K is indicative of Cr(III) easy uptake from the solution (n greater than unity) with high adsorptive capacity. The estimation of the correlation coefficients for Cr(VI) showed that the experimental points fit better to Langmuir model. Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecule is present on the adsorption surface, and the energy of adsorption is constant and there is no migration of adsorbate molecule in the surface plane.

Characterization of metals in biomass

The red rose waste biomass was analyzed for trace metals. The results revealed the traces of other metals in the biomass. The concentrations of the trace metals in the waste biomass were (mg/g): Na(4.81); K(3.14); Li(1.54); Cu(0.005); Zn(0.009); Pb(0.07); Cr(0.23); Co(0.01); Fe(0.24); Mg(0.17) and Mn(0.10).

Effect of pretreatment on *Rosa gruss an teplitz* (red rose) waste biomass

The sorption capacities (mg/g) of non-treated, physically and chemically modified biomass were in the following order for Cr(III): Na-alginate (55.55) > HNO_3 (53.12) > NaOH (50.25) > $(NH_4)_2SO_4$ (49.87) > acetone (49.72) > H_2S (48.31) > EDTA (47.91) > Boiled (47.72) > $CaCl_2$ (47.19) > $Al(OH)_3$ (45.77) > κ-carrageenen (44.57) > native (44.44) > CO_2 (43.05) > Ca-alginate (42.99) > PEI (42.12) > HCl (38.17) > ethanol (36.55) > glutaraldehyde (36.15) > H_2SO_4 (36.07) > HCHO (34.25) > heated (34.16) > CH_30H (34.07) > potash alum (33.55) > Triton-X-100 (32.35) > PEI + glutaraldehyde (29.79) > *Moringa Olifera* (29.79) > benzene (28.44) while the sorption capacities (mg/g) of non-treated, physically and chemically modified biomass were in the following order for Cr(VI): Na-alginate (57.68) > boiled (57.6) > HNO_3 (57.34) > *Moringa*

Olifera (57.08) > HCHO (56.36) > glutaraldehyde (56.32) > CO_2 (56.14) > $CaCl_2$ (55.28) > potash alum (54.72) > PEI (54.72) > NaOH (54.54) > CH_3OH (54.38) > PEI + glutaraldehyde (54.0) > HCl (53.96) > Triton-X-100 (53.96) > benzene (53.3) > $Al(OH)_3$ (53.3) > heated (53.06) > ethanol (52.5) > H_2SO_4 (51) > EDTA (50.02) > H_2S (47.88) > acetone (47.66) > Ca-alginate (47.44) > native (47.29) > $(NH_4)_2SO_4$ (45.2) > κ-carrageenen (45.04) (Fig. 8)

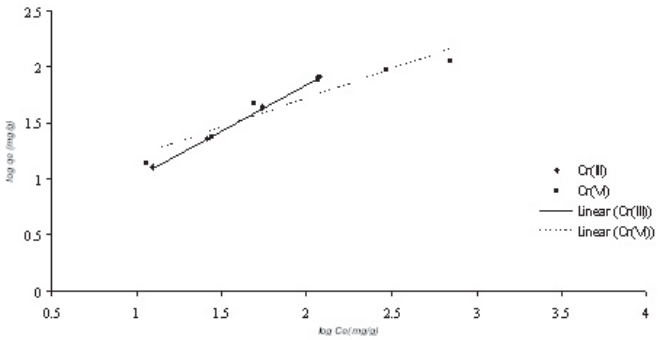

Figure 7: Linearlized Freundlich isotherm models for the sorption of Cr(III) and Cr(VI) by *Rosa gruss an teplitz* (red rose) waste biomass.

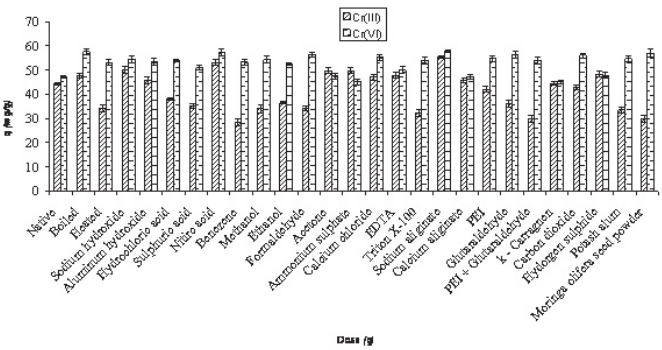

Figure 8: Effect of pretreatments of *Rosa gruss an teplitz* (red rose) waste biomass on the sorption of Cr(III) and Cr(VI).

Physical modifications of biomass remove mineral and organic matter from biomass. Heating of biomass, results in decomposition of organic matter, which results in increase in biomass metal capacity due to availability of more biosorption sites. The increase was attributed to the exposure of the latent binding sites after pretreatment [40]. Preheating of biomass could cause a loss of amino-functional groups from its surface through the nonenzymic Browning reaction. Amino-functional groups are among the functional groups in the composition of polysaccharides which contribute to the binding of heavy metals [41, 42]. Heating may damage the functional groups present on cell wall of biomass and subsequently decrease in metal sorption capacity of biomass will be observed. Preheating of biomass may also cause decomposition of inorganic species which will result in increase in sorption capacity. Boiling remove mineral matter by dissolving it whereas heating remove organic and mineral matter by decomposing it, the subsequent result is introduction of more sorption sites on biomass surface. The results of present study indicated that increase in sorption capacity of *Rosa gruss an teplitz* waste biomass was not only dependent on the nature of biomass but also related to oxidation state of metal. HNO_3 presented more increase in adsorption capacity as compared to HCl and H_2SO_4. This might be due to solubility of more mineral matter of *Rosa gruus an teplitz* biomass in HNO_3, which introduced more porosity in biomass due to increased cellular mass and resulted in enhancement of Cr uptake capacity of biosorbent. However, after a certain concentration of an acid the electronegativity of biomass will decrease due to remaining H^+ ions on the acidic pretreated biomass, may change the biomass electronegativity, resulting in a reduction in biosorption capacity [42-44]. The difference in results after a specific pretreatment may be attributed to the specific type of interaction between the biomass and chemical used for pretreatment, as well as the oxidation state of the metal.

Alkali treatment of biomass may destroy autolytic enzymes that cause putrefaction of biomass and remove lipids and proteins that mask reactive sites. Removal of impurities from surface and rupturing of cell-membrane is reason behind the increase in metal uptake capacity of biomass after basic pretreatment [45-49]. Besides this, the pretreatment could release polymers such as polysaccharides that have a high affinity towards certain metal ions [44]. As NaOH is a stronger base, it removes H^+ ions from the surface of biomass resulting in excess of negative charge introduced on cellular surface [16] which attracts more Cr ions from aqueous solutions. Some researchers also reported that alkali pretreatment significantly enhanced biosorption capacity in comparison with non-treated biomass [42, 50-52]. Rose biomass was also pretreated with gases. Biosorption capacity of biomass after H_2S treatment increased because H_2S forms sulphonic acid in acidic medium. Sulphonic acid is a weak acid and caused the negative charge on the polymer structure of biomass surface due to ionization of organic and inorganic groups. And a more electronegative charged biomass has a more ability to absorb metal. Thus the Cr(III) and Cr(VI) sorption capacity of *Rosa gruss an teplitz* biomass increased after pretreatment with H_2S. The other reason behind this increase is that when H_2S was passed through the aqueous solution of biosorbent it increased the surface area due to increase in porosity of biomass and this uptake capacity of biomass was enhanced. In the case of CO_2 treatment the sorption capacity of biomass may increase or decrease because CO_2 form carbonic acid solution in aqueous phase. Carbonic acid thus formed during pretreatment of biosorbent may affect the metal uptake capacity of biosorbent being treated. The increase or decrease in sorption capacity of biomass after weak acid pretreatment can be attributed to the effect played by polymeric structure of biomass, concentration of weak acid and oxidation state of metal.

The alginates have been found to change the overall sorption capacity of biomass [53-55]. Na-alginate exhibited the better overall ability to remove Cr(III) and Cr(VI) in comparison to native biomass. This may be due to adsorption of Na-alginate on biomass surface and Na-alginate has ability to adsorb metals. Ca-alginate is polymer having carboxylic group responsible for metal binding [53]. Ca stabilizes the biomass by binding alginate and converting it to the gel state thus resultantly sorption capacity was increased. *Rosa gruss an teplitz* biomass was further pretreated with co-agulants. *Moringa Olifera* is a natural coagulant while potash alum is a chemical coagulant. The coagulants have ability to precipitate inorganic or organic material from biomass cells. Thus, metal uptake capacity of any biomass may increase or decrease. The results of present study demonstrate that the metal interactions with coagulant pretreated biomass of *Rosa gruss an teplitz* were strongly dependent on metal oxidation state. Pretreatment effects on rose biomass for biosorption were also evaluated by treating it with other chemicals. Surfactants are the substances with lyophilic and lyophobic groups capable of adsorbing at interfaces. The adsorption of heavy metals on to the biomass from solutions can be enhanced in the presence of surfactants due to reduced surface tension and increased wetting power. In present investigation, in case of surfactant pretreatment of rose biomass maximum adsorption capacity (mg/g) of Cr(III) by Triton X-100 was 53.96 mg/g. Results also depend upon the oxidation state of metal which may reduce uptake capacity of a biosorbent. Uptake capacity of *Rosa gruss an teplitz* waste biomass increased after pretreatment with EDTA. As EDTA is a strong chelating agent, thus have ability to remove metals already present on biomass surface. Resultantly, more sorption sites became vacant for Cr adsorption. Hence, Cr adsorption capacity of *Rosa gruss an teplitz* waste biomass was increased. Pretreatment using κ-carrageenen resulted in the decrease in the sorption capacity as it caused the dissolution of cell wall of the biomass [56]. Pretreatment of biomass with $CaCl_2$ only slightly enhanced the removal efficiency of Cr(III) and Cr(VI). This enhancement was due to cleaning of biomass surface by calcium ions which might be easily replaced with Cr during biosorption. Park *et al*. [57] also reported similar increase in Cr(VI) biosorption after $CaCl_2$ treatment of *Eclonia* sp. $(NH_4)_2SO_4$ is a protein salting out agent. It can denature protein of cell wall and cause their precipitation. Precipitation may increase or decrease the sorption capacity of a biosorbent. Cr(III) adsorption capacity of *Rosa gruss an teplitz* biomass pretreated with $(NH_4)_2SO_4$ increased. Due to precipitation of protein, cell wall is ruptured which results in more sorption sites and adsorption is enhanced. Cr(VI) adsorption capacity of *Rosa gruss an teplitz* biomass pretreated with $(NH_4)_2SO_4$ decreased. The decrease in sorption capacity can be attributed to disturbance of those functional groups which were involved in Cr(VI) biosorption.

Treatment of the biomass with organic solvents, such as acetone and benzene, slightly enhanced the Cr(VI) uptake capacity of *Rosa gruss an teplitz* waste biomass. Ashkenazy *et al*. [51] found that extraction with organic solvents removes the protein and lipid fractions of the biomass surface. Thus, this treatment might expose more metal binding sites and improve the

adsorptive property of the biomass. However in the present study in case of Cr(VI) the treatment of biosorbent with benzene extracts the lipid fraction of biosorbent [58]. Therefore, the reduction in biosorption efficiency was observed, which reveals that the lipids in the cell wall of *Rosa gruss an teplitz* biomass contribute to Cr biosorption. They attributed the decrease to either lipid extraction or the probable structural changes that may have resulted due to the harsh conditions of the extraction process. The formaldehyde pretreatment increased only Cr(VI) biosorption while decreased Cr(III) biosorption. Huang and Huang [59] suggested that when biomass was pretreated with formaldehyde, methylation of amine groups present in the cell wall may increase or decrease the biosorption capacity which suggests that amine groups play an important role in biosorption. Methanol and ethanol are polar organic solvents. These solvents can cause polarization in biomass which will result in increase or decrease in sorption capacity of a biomass, depending the oxidation state of metal being sorbed. Same results were obtained in the present study. Cr(III) and Cr(VI) uptake capacities of *Rosa gruss an teplitz* biomass decreased and increased respectively after pretreatment with methanol and ethanol. The biomass of *Rosa gruss an teplitz* was modified with polyethylenimine (PEI) and then crosslinked with glutaraldehyde. The crosslinked PEI was chemically bonded on the biomass surface through the amine and carboxylate groups on the rose biomass. The modified biomass with amine groups showed a significant increase in sorption capacity for Cr(VI). Glutaraldehyde was used as a cross-linking agent in an effort to improve the sorption capacity of *Penicillium chrysogenum* during biomass modification using polyethyleneimine (PEI) [60]. The use of glutaraldehyde at a higher concentration resulted in more rigid biomass. So sorption sites are blocked and sorption capacity decreased.

CONCLUSIONS

The present study explored the utilization of *Rosa gruss an teplitz* distillation waste biomass for Cr(III) and Cr(VI) uptake. The results revealed that the biosorption process of Cr(III) and Cr(VI) by *Rosa gruss an teplitz* waste biomass was strongly dependent on experimental parameters. After pretreatment of biomass, the modified structure of the biomass and oxidation state of the chromium play a significant role in determining the metal uptake capacity of the biomass. A maximum uptake capacity of 55.55 and 57.68 mg/g was observed with sodium alginate modified biomass for Cr(III) and Cr(VI) respectively. The Cr(III) and Cr(VI) biosorption data fitted well to Freundlich isotherm and Langmuir model well respectively. The sorption data of Cr(III) and Cr(VI) uptake by *Rosa gruss an teplitz* biomass followed the pseudo-second-order kinetic models.

ACKNOWLEDGEMENTS

Authors would like to thank staff of Rosa Laboratory, Institute of Horticulture Sciences, University of Agriculture, Faisalabad, Pakistan for their cooperation throughout present study.

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