Biosorption of Pb(II) and Co(II) on Red Rose Waste Biomass

Haq Nawaz, Bhatti*+; Rubina, Khadim; Muhammad Asif, Hanif

Environmental Chemistry Laboratory, Department of Chemistry & Biochemistry, University of Agriculture,
Faisalaba-38040, PAKISTAN

ABSTRACT: *In the present investigation the biosorption potential of rosa gruss an teplitz (Red Rose) Waste Biomass (RRWB) for the removal of Pb(II) and Co(II) from aqueous solutions was studied. The effect of different process parameters such as pH, biosorbent dose, biosorbent size, temperature, contact time, initial metal concentration and pretreatments on the biosorption capacity of this waste biomass was studied. The results showed that the equilibrium data for both metal ions followed the Langmuir isotherm with a biosorption capacity of 112.0 and 115.9 mg/g for Pb(II) and Co(II) respectively. The overall biosorption process was best described by pseudo-second-order kinetics. Modification of red rose waste biomass by pretreating with different reagents significantly improved its biosorption capacity. A maximum biosorption capacity of 99.72 and 51.68 mg/g was observed for Pb(II) and Co(II) by treating the biomass with methanol and polyethyleneimine + glutraldehyde respectively. The results clearly indicated that red rose waste biomass has a potential to remove heavy metals from aqueous solutions.*

KEY WORDS: *Rosa gruss an teplitz, Waste biomass, Pretreatments, Kinetics, Biosorption.*

INTRODUCTION

Heavy metals are extensively used in industries like electroplating, paint pigments, basic steel works, metal finishing, electrical accumulators, batteries etc. These metals cannot be degraded biologically into harmless products to avoid serious health hazards and are mostly disposed in water [1]. The contamination of water by toxic heavy metals is a world wide environmental problem. Pb(II) and Co(II) are toxic metals due to their conservative and cumulative chararecteristics. The major sources of Pb(II) discharge into environment are automobile exhaust, paint coloration and particulate matters. Excessive amount of Pb(II) in human can cause anemia, hypertension and brain damage [2,3]. Industrial exploitation of Co(II) in alloy production, electroplating, generation of gas turbines and petrochemical industries [4], results

in discharge of Co(II) wastes into the environment leading to variety of toxic effects on all living organisms including plants, animals and microorganisms [5]. It also causes neurotoxicological disorders and genotoxicity in human beings and in chronic cases may cause cancer [6].

Conventional methods for removing heavy metals from aqueous solutions suffer some drawbacks such as high operational cost and sludge problem [7-10]. Treatment of effluents and ground water polluted with heavy metals following biotechnological approaches is simple, relatively inexpensive and provides full-scale remediation over existing physico-chemical technologies [11]. Biosorption is a potential attractive technology for removal of heavy metal ions that utilizes low-cost biosorbents [12]. Both living as well as non-living

microbial biomasses can act as effective metal accumulator, but use of dead biomass is preferred since it is easy to handle, processes are growth independent and possess no harm while using pathogenic strains [13]. Modification of a biomass using different pretreatment methods such as heating, autoclaving, freezing, drying, boiling and chemical pretreatment showed enhancement or reduction in metal biosorption [14,15].

Rosa gruss an teplitz (red rose) is an important shrub cultivated everywhere in the world because of its florist's demand. It is among the most extensively used flowers for steam distillation. Rose waste is also obtained as a by-product during distillation having no commercial importance. In the present study, waste biomass of red rose was exploited for removal of Pb(II) and Co(II) from synthetic effluents.

EXPERIMENTAL SECTION
Biomass collection and preparation

Red Rose Waste Biomass (RRWB) was obtained from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan and was extensively washed with distilled water to remove particulate material from its surface, and oven dried at 60 °C for 72 h. Dried biomass was ground using food processor (Moulinex, France). The dried biomass was sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain homogenous biomass with desired particle size.

Reagents

All chemicals used were of analytical grade and mainly purchased from purchased from E. Merck Company (Darmstadt, Germany) except *Moringa Olifera* seed powder which was purchased from local market.

Pb(II) and Co(II) solutions

Stock Pb(II) and Co(II) solutions (1000 mg/L) were prepared by dissolving 1.598 g Pb(NO$_3$)$_2$ and 3.10 g Co(NO$_3$)$_2$ in 1000 mL of Double Distilled Water (DDW). Pb(II) and Co(II) solutions of different concentrations were prepared by adequate dilution of stock solution with DDW.

Batch biosorption studies

Batch biosorption studies were carried out using fixed volume (100 mL) of Pb(II) and Co(II) solutions, desired biosorbent dose (0.05, 0.1, 0.2, 0.3 and 0.4 g) and size

(< 0.25, 0.25-0.35, 0.35-0.50, 0.50-0.71 and 0.71-1.0 mm) at 30 °C for 24 h. To study the effect of pH (1-7), initial metal concentration (25, 50, 100, 200, 400 and 800 mg/L) and contact time (15, 30, 60, 120, and 240 min), different experiments were also performed. 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).

For physical pretreatments, the biomass was heated in an oven and boiled (biomass was boiled in 95 mL of water). In case of chemical treatments, 5 g of finely divided rose biomass was soaked in 100 mL of respective reagent for 1 h as reported earlier [14, 15]. The suspensions were extensively washed with DDW and filtered thoroughly. Finally the resulting biomass was oven dried at 60°C for 48 h to constant weight.

Determination of the Pb(II) and Co(II) contents in the solutions

The concentrations of Pb(II) and Co(II) in the solutions before and after biosorption were analyzed by Perkin-Elmer AAnalyst 300 Atomic Absorption Spectrometer equipped with an air-acetylene burner and controlled by Intel personal computer.

Metal uptake capacity and % removal

The Pb(II) and Co(II) uptake capacity of biomass was calculated by the simple concentration difference method. Biosorption capacity "q_e" is amount of metal ion (mg) biosorbed per g (dry weight) of biomass. The following equations were used to compute the metal uptake capacity (Eq. (1)) by the sorbent and % metal sorption (Eq. (2)):

$$q_e = V\,(C_i - C_e)\,/\,1000W \tag{1}$$

Where V is the volume of the solution in mL and W is the mass of the sorbent in g, C_i (mg/L) and C_e (mg/L) are the initial and equilibrium metal concentrations, % sorption is given as

$$\% \text{ sorption} = (C_i - C_e)\,/\,C_i \times 100 \tag{2}$$

All data represent the mean of three independent experiments. The results are reported as mean ± standard deviation.
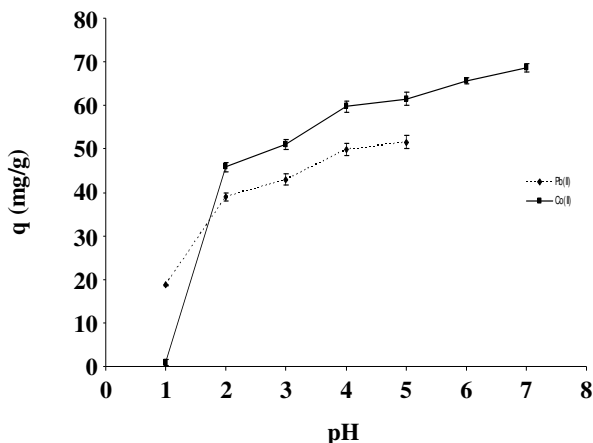
82

Fig. 1: Effect of pH on uptake of Pb (II) and Co (II) by RRWB.

Fig. 2: Effect of biosorbent size on uptake of Pb(II) and Co(II) by RRWB

RESULTS AND DISCUSSION
Effect of pH

The results regarding the effect of pH on the metals uptake capacity of RRWB are depicted in Fig. 1. The results revealed that RRWB possessed maximum biosorption capacity of 51.53 and 68.67 mg/g for Pb(II) and Co(II) respectively at pH value 5 and 7, while the removal percentage of Pb (II) and Co (II) were 49.77 and 67.7, respectively. Lower or high pH has resulted either in low biosorption or precipitation of the corresponding metal ions. Studies have shown that precipitation of salts occurred at pH 6 for Pb(II) and 8 for Co(II) so adsorption studies were meaningless above pH 5 and 7 [16]. The removal of metal ions from aqueous solution by adsorption depended on the pH of solution, as the latter affected the surface charge of biosorbent, solution chemistry of metals, activity of functional group in the biomass, the degree of ionization and the species of adsorbate [17]. Due to high proton concentration at lower pH, metal ion biosorption decreases due to the positive charge density on metal binding sites, i.e. hydrogen ions compete effectively with metal ions for binding. The negative charge density on the cell surface of the biosorbent increased with increasing pH due to deprotonation. The metal ions then compete more affectively for available binding sites, which increased the biosorption [18, 19]. The selection of the optimum pH must take into account for proper sorption of the metal ions. The results revealed that sorption decreased at low pH values.
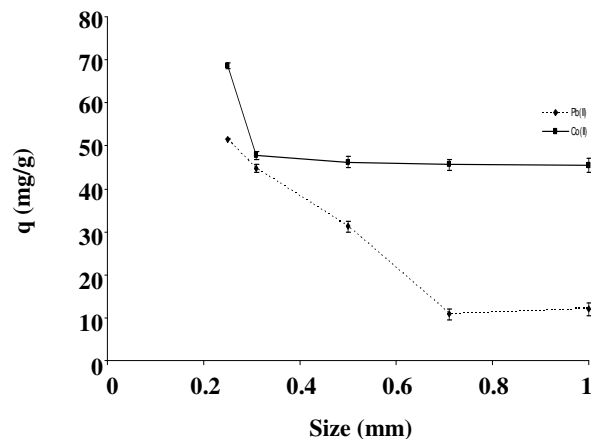
Effect of biosorbent size

The results of the effect of biosorbent size on Pb(II) and Co(II) biosorption are shown in Fig. 2. Maximum biosorption capacity (51.53 mg/g) of RRWB was observed with particle size 0.25 mm. Similarly, the same particle size (0.25 mm) also resulted in maximum biosorption capacity (115.42 mg/g) of Co(II) from the aqueous solution. Smaller sizes provide the greater surface area, which result in an increase in the binding sites of the biosorbent [10, 20, 21].

Kinetic studies

The effect of the contact time on the biosorption of Pb (II) and Co (II) on RRWB was studied up to 1440 min. The results revealed that maximum biosorption capacities for Pb(II) and Co(II) were achieved generally in first 30 min, initially biosorption takes place very rapidly and then it continued at slower rate up to maximum sorption. The equilibrium reached after 4 h. Thus subsequent biosorption experiments were performed using the optimum contact time required to reach equilibrium of each metal ion.

Kinetic modeling

A kinetic study with fixed metal ion concentration and biosorbent dose was performed at various time intervals. Kinetics of biosorption has been widely tested by first order expression given by Lagergren [22] and pseudo-second-order approach. The first order Lagergren equation is

83

Table 1: Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Co(II) and Pb (II) sorption by RRWB.

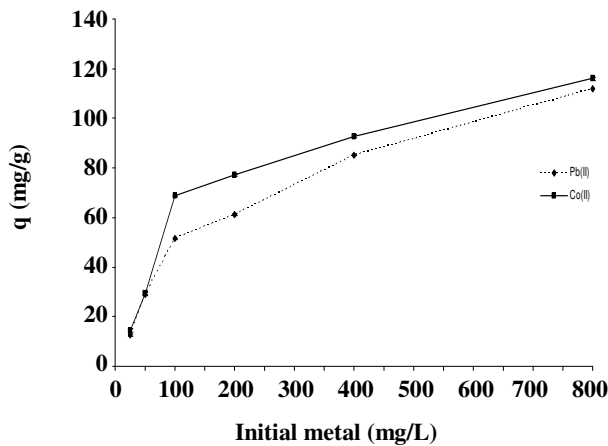| Metal	Pseudo first order Kinetic model			Experimental value	Pseudo second order kinetic model		
	q_e (mg/g)	$K_{1,ads}$ (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	$K_{2,ads}$ (g/mg.min)	R^2
Pb	21.62	0.0244	0.949	53.26	53.47	2.51x10^{-3}	0.99
Co	5.66	0.170	0.717	68.67	72.46	2.77x10^{-4}	0.91

Fig. 3: Effect of initial metal concentration for uptake of Pb(II) and Co(II) by RRWB.

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads} t}{2.303} \qquad (3)$$

The pseudo- second- order equation is

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{t}{q_t} \qquad (4)$$

where q_e is the mass of metal absorbed at equilibrium (mg/g), q_t the mass of metal at time t (min), k_1,ads the first order reaction rate constant of adsorption (per min), k_2,ads the pseudo-second-order rate constant of adsorption (mg/g min). A comparison between Lagergren pseudo-first order and to pseudo-second-order kinetic models are tabulated in Table 1. The Lagergren first-order rate constant (k_1, ads) and q_e determined from the model indicated that this model failed to estimate q_e since the experimental values of q_e differed from those estimated. The correlation coefficients for the first order kinetic model obtained at various time intervals are lower than the second order rate equation. A high degree of correlation coefficient was obtained for the second order kinetic model. The results suggest that the sorption system followed the second order kinetics.

Effect of initial metal ion concentration

The sorption of metal ions depends on the available sites of the biosorbents and hydrated radius of the ions. The effect of initial metal ions concentration is depicted in Fig. 3. Sorption of both Pb(II) and Co(II) ions increases with increase in metal concentration. Sorption characteristics indicate that surface saturation is dependent on initial metal ion concentration, which increases with concentration. Maximum uptake capacity of RRWB was recorded with 800 mg/L for both metals, which is generally the maximum concentration of metal ions in the wastewater. The results clearly demonstrated that RRWB has greater affinity for both metal ions.

Adsorption isotherms

The Langmuir and Freundlich isotherms were used to represent the equilibrium relationship for different initial Pb(II) and Co(II) concentrations in order to understand the sorption process. This sorption characteristic indicated that surface saturation is dependent on the initial metal ion concentrations. At low concentrations adsorption sites took up the available metal ions more quickly. However at higher concentrations metal ions need to diffuse to the biomass surface by inter particle diffusion and greatly hydrolyzed ions diffuse at slower rate. If the metal ions were taken up independently on single type of binding site in such a way that the uptake of first metal ions does not affect the sorption of next ions, then the sorption process would follow the Langmuir adsorption isotherm Eq. (5)

$$C_e/q_e = 1/q_{max}.K_L + C_e/q_{max} \qquad (5)$$

Where
q_e = equilibrium adsorption capacity.
C_e = equilibrium concentration.
q_{max} = maximum adsorption capacity and K_L is constant.

The Freundlich equation is another model which has been commonly used to describe adsorption isotherm. Its linear form is represented by Eq. (6).

Table 2: Comparison of Langmuir and Freundlich isotherm parameters for Co (II) and Pb (II) uptake by RRWB.

Metal	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	q_{max} (mg/g)	K_L (L/mg)	R^2	q_e (mg/g)	q_{max} (mg/g)	K (mg/g)	1/n	R^2
Pb(II)	125	9.9×10^{-3}	0.98	112.0	129.02	5.66	0.478	0.89
Co(II)	125	0.014	0.99	115.9	140.89	8.19	0.436	0.79

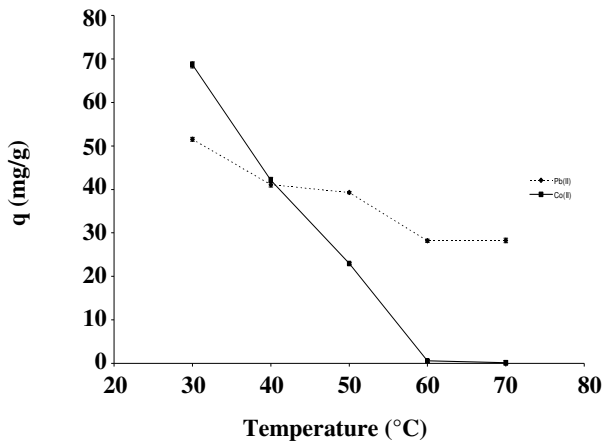***Fig.4: Effect of temperature for uptake of Pb(II) and Co(II) by RRWB.***

Fig. 5: Effect of pretreatments on uptake of Pb(II) and Co(II) by RRWB.

$$\text{Log } q_e = \log K + 1/n \log C_e \qquad (6)$$

Where

q_e = the amount adsorbed per unit mass of adsorbent.

C_e = equilibrium concentration.

K and 1/n are constants obtained from regression equation called intercept and slope respectively. It was found that sorption equilibrium data were better fitted by the Langmuir isotherm in the concentration range studied. The Freundlich equation is an empirical relationship describing the adsorption of solutes from liquid to the solid surface. Table 2 clearly showed the lack of fit the data for Freundlich isotherm model as indicated by a large scatter of the experimental points from the line of best fit.

Effect of temperature

The effect of temperature on the removal of Pb(II) and Co(II) by RRWB from aqueous solution was studied by varying the temperature between 30 to 70 °C. Maximum removal uptake of Pb(II) and Co(II) was obtained at 30 °C. The results showed that adsorption of metal ion by RRWB decreased with increase in temperature (Fig. 4). The biosorption of Pb(II) and Co(II) ions
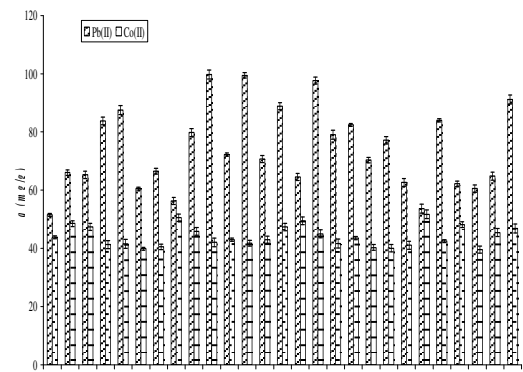
by RRWB seems to be the diffusion of metals on the surface of biomass. Increasing the medium temperature decreases metal uptake capacity by RRWB. Results indicated that metal–biosorbent adsorption process is exothermic in nature [14, 16, 23].

Effect of pretreatments

The values of sorption capacity (mg/g) of native, physically and chemically modified RRWB (Fig. 5) were found in the following order for Pb(II): methanol (99.72) > formaldehyde (99.46) > EDTA (97.6) > *Moringa olifera* seed powder (91.14) > ammonium sulphate (88.88) > aluminum hydroxide (87.5) > κ-carragnen (84.01) > sodium hydroxide (83.77) > Na-alginate (82.41) > benzene (79.76) > Triton X-100 (79.01) > PEI (77.13) > ethanol (72.2) > acetone (70.66) > Ca-alginate (70.32) > H_2SO_4 (66.5) > boiled (66.02) > heated (65.28) > potash alum (64.85) > $CaCl_2$ (64.51) > glutaraldehyde (62.64) > CO2 (62.17) > HCl (60.52) > hydrogen sulphide (60.52) > HNO_3 (56.31) > PEI + glutaraldehyde (53.6) > native (51.53). On the other hand , this order for Co(II) was: formaldehyde (88.04) > glutaraldehyde (86.72) >

85

Triton X-100 (83.46) > CaCl$_2$ (82) > heated (78.8) > ethanol (77.5) > sodium hydroxide (74.38) > hydrogen sulphide (71.73) > boiled (70) > κ-carragnen (69.68) > Ca-alginate (69.68) > aluminum hydroxide (68.70) > native (68.67) > potash alum (66.73) > PEI (64.66) > acetone (64.65) > CO2 (64.45) > PEI + glutaraldehyde (63.35) > HNO$_3$ (62.2) > methanol (59.94) > benzene (57.75) > HCl (54.8) > H$_2$SO$_4$ (52.43) > EDTA (46.33) > Na-alginate (46.27) > *Moringa olifera* seed powder (45.8) > ammonium sulphate (40.12).

An increase in biosorption of Pb(II) ions as a result of pretreatment could be due to an exposure of active metal binding sites embedded in the cell wall or chemical modifications of the cell wall components. *Huang & Huang* [24] reported that the increase in metal biosorption after pretreating the biomass could be due to the removal of surface impurities and to the exposure of available binding sites for metal biosorption.

Pretreatments showed a significant effect on the uptake capacity of RRWB Physical and chemical pretreatments either increased or decreased the uptake capacity of biosorbents [15, 24]. Boiling of the biomass removed mineral matter from biomass and introduces more sorption sites on biomass surface hence sorption capacity has increased [25]. Heating of biomass, results in decomposition of organic matter while boiling remove mineral matter by dissolving it, the subsequent result is introduction of more sorption sites on biomass surface, and hence sorption capacity increased [26].

Fig. 5 illustrates that pretreatment with all of the chemicals enhanced the sorption of Pb(II) ions, whereas, sorption of Co(II) decreased when pretreated with Al(OH)$_3$, potash alum , PEI , acetone , CO$_2$, PEI + glutaraldehyde , HNO$_3$, methanol , benzene , HCl , H$_2$SO$_4$, EDTA , (NH$_4$)$_2$SO$_4$, *Moringa olifera* seed powder and Na-alginate. For Pb (II), acidic pretreatments increased the sorption capacity of the RRWB. Similar results were also reported by *Kapoor & Viraraghavan* [27]. They reported that acid pretreatment slightly increased the biosorption capacity of *A. niger*. In case of Co(II), the sorption capacity decreased after acid pretreatment. A specific pretreatment resulted in specific change that might be due to the specific interaction between the biomass and the chemical used for that treatment. Increase or decrease in the sorption capacity of a particular biomass after acidic pretreatment involves

two factors: (i) the polymeric structure of biomass surface exhibits a negative charge due to the ionization of organic groups and inorganic groups. Biomass having the higher electronegativity will have the greater attraction and adsorption of heavy metal ions. However, after a certain concentration of an acid, the electronegativity of the biomass would decrease due to remaining H$^+$ ions on the acidic pretreated biomass, may change the biomass electronegativity, resulting in a reduction in biosorption capacity [27-29] (ii) At a certain concentration, acids can enhance uptake capacity of biomass by increasing the surface area and porosity of original sample [28 , 30].

When RRWB was pretreated using bases, the sorption capacity increased as reported earlier [31]. The alkali pretreatment is an effective method to improve the metal biosorption capacity of dead biomass. Alkali pretreatment can increase the biosorption of heavy metals by destroying autolytic enzymes causing putrefaction of biomass, remove lipids and proteins that mask binding sites and could release certain biopolymers from the cell wall that have a high affinity towards heavy metal ions [29]. For both metals i.e., Pb(II) and Co (II), after NaOH pretreatment, biosorption capacity significantly enhanced. The residual alkalinity in biomass may also result in increased hydrolysis of certain metal ions and thereby enhance overall metal ion emoval by the treated biomass [32]. The pretreatment released polymers such as polysaccharides that have a high affinity towards certain metal ions [33].

Alginate is produced from algin, a high molecular weight polymer composed of D-mannuronic acid and L-guluronic acid, when the protons of the carboxylic groups are replaced by metal ions [34]. Previous studies showed that alginates exhibited the best metal-sequesting ability. Change in the cell wall composition of red rose waste caused by these chemicals may attribute the difference in results after alginic pretreatment. Calcium stabilizes the biomass by binding alginate and converting it to the gel state, so the sorption capacity was increased. Calcium alginate is a polymer and carboxylate group of this alginate has been identified as the main binding site [35]. By comparison, pretreatment using Na-alginate caused a decrease in the Co(II) sorption capacity which may be explained as after treatment Na$^+$ may remain on the cell wall of biomass and may be in competition with the investigated heavy metal on the binding sites of the cell wall.

Triton X-100 removes oily phase from the cell surface hence increases the sorption capacity. Triton X-100 is a non-ionic surfactant. Surfactants are the substances with lyophilic and lyophobic groups capable of adsorbing at interfaces. The biosorption of heavy metal ions to the biomass can be enhanced in the presence of surfactants due to reduced surface tension and increased wetting power [36].

CONCLUSIONS

The results indicated that maximum biosorption of Pb(II) and Co(II) by RRWB was observed at pH 5 and 7 respectively. The equilibrium data for both metal ions followed the Langmuir isotherm. Kinetic data was better described by pseudo-second order model. A maximum biosorption capacity of 99.72 and 51.68 mg/g was observed for Pb(II) and Co(II) by treating the biomass with methanol and polyethyleneimine + glutraldehyde respectively. The results clearly indicated that red rose waste biomass has a potential to remove heavy metals from aqueous solutions.

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