

## Biosorptive removal of cobalt from aqueous solution by using native and thiourea modified *Pennisetum glaucum*

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### ABSTRACT

The purpose of this investigative research is to find the acceptable solution for the removal of Co(II) by using native and modified *Pennisetum glaucum*. Comparison of biosorption parameters for native and modified material confirmed the promising efficiency of modified material due to active functionalities and exposed surface area. Physiological characteristics were observed by SEM, EDX and FT-IR analysis. Biosorption batch process was performed as function of biosorbent dose, contact time, initial Co(II) ion concentration, solution temperature and pH. Experimental data was investigated by known isothermal models. The Langmuir isotherm fitted well and the RMSE value was calculated using the non-linear approach. Kinetic studies followed the pseudo-second order and thermodynamic parameters ensured the appreciable biosorption behavior of thiourea modified *Pennisetum glaucum*.

*Keywords:* *Pennisetum glaucum*; Biosorption; Kinetic studies; Thermodynamic; Thiourea

### 1. Introduction

Cobalt is a rare lustrous silver metal and present in the earth crust in chemically combined form. The most important cobalt minerals are cobaltite and smaltyn. It is a trace dietary mineral as it is component of cabalamin (Vitamin B<sub>12</sub>) [1]. But anthropogenic activities are alarmingly increasing its concentration in the environment. Cobalt is used in prosthetic surgeries [2], dental alloy and implant component [3,4], colored glass formation [5] permanent magnet formation [6], alloy formation [7] and nickel cobalt battery

[3]. Moreover it is used as catalyst [8,9], pigment formation [10], metallurgy and electroplating [11].

The increasing concentration of cobalt is heading towards cobalt poisoning. Radioactive isotope of cobalt is present in metals used in nuclear reactor and also present in the discharged effluent [12]. Cobalt may cause contact dermatitis [13], mutagenic changes (cancer) and cardiomyopathy [14]. Cobalt intake may affect sensory system and gastrointestinal tract, low blood pressure, paralysis, genetic and bone defects [15,16].

Many techniques have been applied over the years and are still being tested to remove heavy metals from aqueous

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solution including chemical precipitation [17], ion exchange [18], membrane filtration, coagulation, floatation and electrochemical method. Sorption is a process in which ions from solution phase transfer to solid phase where they are bound by physical or chemical interactions. Various ionic sorbents like zeolite [19], Kaolinite [20], activated carbons [21], granular sludge [22] are used for the removal of metal ions from water. Biosorbents are in demand due to their multiple advantages over other sorbents. Biosorbents for the removal of metal ions are microorganisms like bacteria [23], algae [24], yeast [25] and molds [26] while agricultural wastes are the other preferable biosorbent due to their availability and economic advantages. Agricultural biosorbents include rice husk [27], wheat straw [28], corn cob [29] sugarcane bagasse [30]. Researchers are reporting the physical and chemical methods to improve the biosorption capacity of the biosorbents. Chemical modification causes the surface chemistry of biosorbents to alter by addition or modification of new or already present functional groups. The addition of groups that can act as chelating agents is more preferable.

Present research study aims at the modification of *Pennisetum glaucum* by thiourea and its comparison with unmodified plant biomass to draw a conclusion for the effective biosorbent for the removal of Co from aqueous solution. Process parameters of biosorption study were carried out for both modified *Pennisetum glaucum* (MPG) and unmodified *Pennisetum glaucum* (UPG). Biosorption equilibrium study was comprehended by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. Biosorption mechanism is elaborated by Kinetic models and thermodynamic parameters.

## 2. Material and methods

### 2.1. Collection and thiourea modification of *Pennisetum glaucum*

*Pennisetum glaucum* was collected from a field of south Punjab, Pakistan (30°19'60" N and 72°48'0" E). Plant biomass was dried and washed with double distilled water to remove dust and other water soluble impurities. It was grinded and sieved by using 200–250 µm mesh sieve. It was washed and dried in oven at 60°C. The material obtained was designated as unmodified *Pennisetum glaucum* (UPG). The dried biomass was mixed with thiourea (Riedel-de-Haen) in 1:2 ratio and homogenized on orbital shaker (Wisd, SHO 2D) for 24 h and heated for 15 min at 60°C. It was filtered, washed and dehydrated in oven at 60°C. This material is designated as modified *Pennisetum glaucum* (MPG).

### 2.2. Characterization of biosorbents

UPG and MPG biosorbents were characterized by Fourier Transform Infrared (FTIR) scanned at 650–4000/cm for the identification of functional group present on the surface. Complete surface analysis was determined by Scanning Electron Microscope (SEM, FEI Nova Nano SEM 450) and elemental analysis was performed by Energy Dispersion X-ray spectroscopy (EDX, Nova SEM).

### 2.3. Batch biosorption studies

Biosorption study of Co by UPG and MPG was studied by using batch stirred biosorption experiment comprises of process parameters like biosorbent dose, contact time, initial pH and temperature. Each parameter was performed independently by keeping all other parameters constant. The slurry was homogenized by using orbital shaker (SHO-2D) at 100 rpm. After the batch parameters experimental steps concentration of Co was determined by using atomic absorption spectrophotometer (AAS, Perkin Elmer Analyst 100). The removal percentage and biosorption uptake capacity ( $q_e$ , mg/g) for Co both by UPG and MPG was determined by consideration of initial ( $C_i$ , mg/L) and equilibrium metal ion concentration ( $C_e$ , mg/L) by using Eqs. (1) and (2), respectively.

$$\text{Removal percentage(\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q_e (\text{mg/g}) = v \times \frac{(C_i - C_e)}{m} \quad (2)$$

where 'v' (mL) is the volume of solution under study, and 'm' (g) is the mass of biomass taken either of UPG or MPG.

Biosorbent dose was varied in range from 0.1 g/50 mL to 1 g/50 mL for both UPG and MPG plant biomass. pH step was studied with variation 1 to 9 for the selection of best suitable pH range for the removal of Co metal ions. Contact time was studied in range 5–45 min with the difference of 10 min between two values. Effect of temperature was investigated under temperature range 10–40°C. Controlled blank experiment was performed for the accuracy of each experimental step which is further performed in triplicate fashion. Microsoft Excel 2013 program was used for evaluation of obtained data in the form of graphs and  $R^2$  was considered as investigation criteria for specific mathematical models. Errors in the predicted models were determined by root mean square error by using following formula

$$\text{RMSE} = \sqrt{\frac{\sum (q_{e(\text{cal})} - q_{e(\text{exp})})^2}{N}} \quad (3)$$

where  $q_{e(\text{cal})}$  and  $q_{e(\text{exp})}$  represent the calculated and experimental uptake capacity of used biosorbent.  $N$  shows the number of data points in each step.

## 3. Result and discussion

### 3.1. Biosorbent characterization

Characteristic functional groups are responsible for the active binding sites for metal ions to govern the biosorption process. Unmodified *Pennisetum glaucum* (UPG) showed the characteristic peaks at 1037, 1242–1246, 1316–1321 and 2922  $\text{cm}^{-1}$  as shown in Table 1. Etherial functional group is observed by peak at 1037  $\text{cm}^{-1}$  and unsaturated ether and stretching frequencies of carboxylate ions are observed at 1242–1245  $\text{cm}^{-1}$  [31]. –C–H stretch and dimer –OH in carboxylic acid is observed at 2922  $\text{cm}^{-1}$  [32].

Thiourea modified *Pennisetum glaucum* (MPG) showed addition peaks at 729 and 1610  $\text{cm}^{-1}$  along with peaks at

Table 1  
Characteristic functional groups of unmodified and modified *Pennisetum glaucum*

Unmodified <i>Pennisetum glaucum</i>		Modified <i>Pennisetum glaucum</i>	
Peaks/cm	Bonds	Peaks cm <sup>-1</sup>	Bonds
1037	C-O-C	729	C-H def S-O stre
1242–1246	O=C-O- stre	1032	C-O-C
1316–1321	CH <sub>2</sub> vib	1406–1460	Broden CH <sub>2</sub> vibr
2922	C-H stre OH dimer	1610	N-H bending
		2922	C-H stre OH dimer

1032, 1406–1460 and 2922 cm<sup>-1</sup> as shown in Table (1). These additional peaks are -C-H deformation of methylene group and -S-O stretching frequency in covalent sulphite [33]. Thiourea provided S to the surface of biomass and formed covalent sulphite which might be an active binding site for metal ions. Another peak which is not present in UPG is at 1610 cm<sup>-1</sup> which represents the -N-H bending carbonyl of amides. Modified material is enriched with N which enhanced the binding character of MPG. It can be inferred that modification enhanced the active binding sites which may increase the biosorption property of the material due to newly inducted functionalities. Additional functional groups of N and S and O provided the chelation site on the surface [34].

Surface of UPG and MPG was analyzed by scanning electron microscopy (SEM). This morphological analysis was helpful for determination of structural changes after thiourea modification of plant biomass. Morphological structure of UPG is less exposed as compared to MPG and this visualization indicated that the surface became more rough after modification. This might be due to incorporation of functional groups during modification procedure thus enhancing the feasibility of attachment of Co metal ions as shown in Fig. 1b. Fig. 1c indicated the Co loaded MPG image, when Co metal ions were attached to MPG Fig. 1b exposed surface became less ruptured and metal ions found attachment sites on the surface.

Energy dispersion X-ray spectroscopy elaborated the elemental analysis. Fig. 2 indicates that calcium and potassium of biosorbent was replaced by Co metal ions when it was dipped in metal ion solution. Co (II) ions found the attachment sited on absorbent and removed from the aqueous solution by ion exchange mechanism. Nitrogen is indicated in MPG but not shown in Co loaded MPG which indicated that nitrogen incorporated by modification process is acted as active binding site and replaced by Co or other anion. Table 2 also describes the incorporation of of Co metal ion on the surface of plant biomass.

### 3.2. Effect of biosorbent dose

Effect of biosorbent dose is well illustrated in Fig. 3. UPG and MPG both materials showed the same increasing

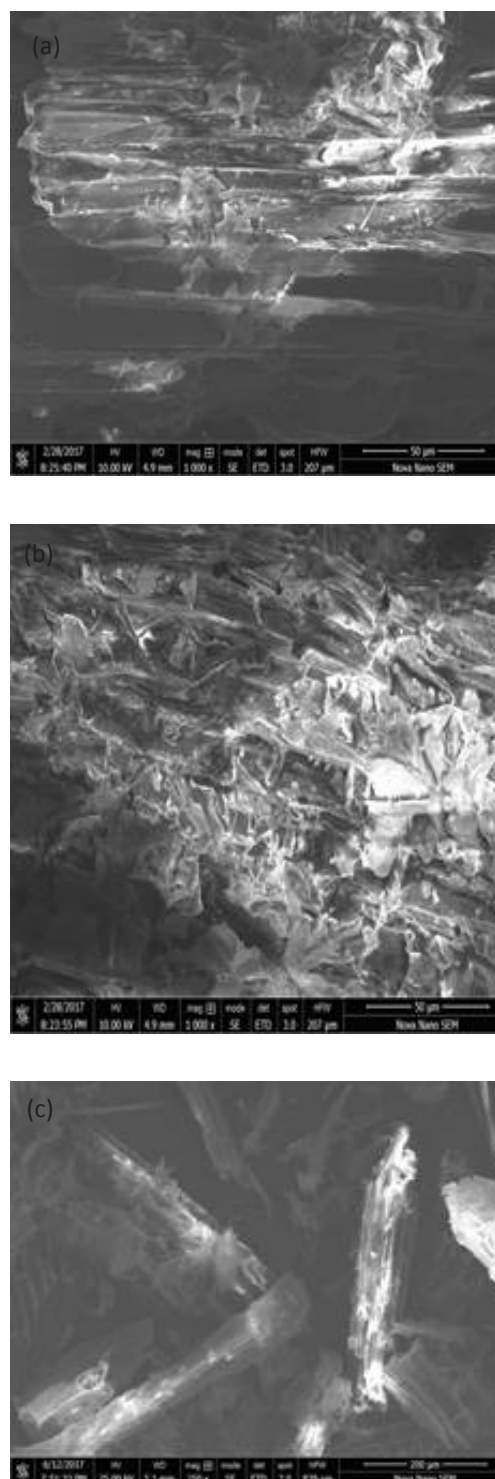


Fig. 1. SEM images of UPG (a), MPG (b) and Co loaded MPG (c).

trend of percentage removal with the increase in amount of biosorbent dosage. Initial concentration of 50 mg/L was set for both biosorbents and their amount was varied from 0.1 to 1 g for the evaluation and comparison of uptake capacity as well as the percentage biosorption efficiency of metal ions. Increasing trend is observed due to more available

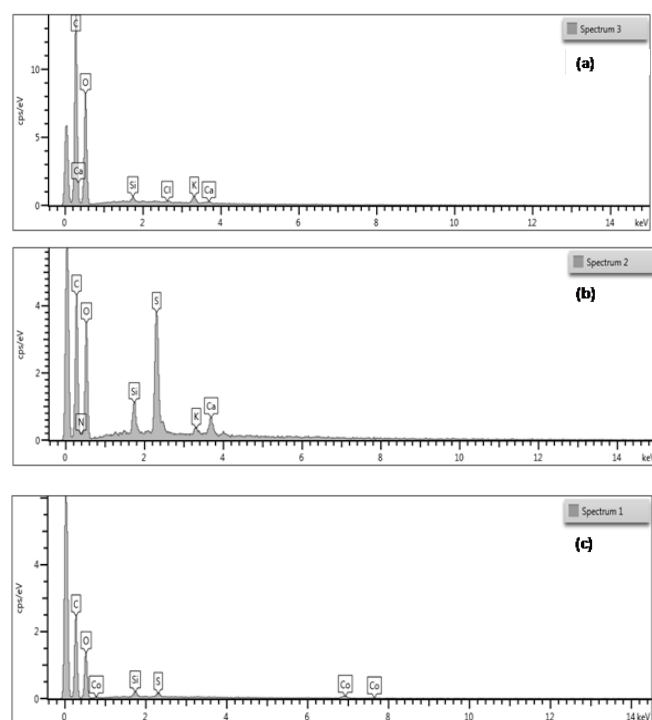


Fig. 2. EDX images of UPG (a), MPG (b) and Co loaded MPG(c).

Table 2  
Elemental analysis of UPG, MPG, Co loaded MPG

Element	Wt%	Wt% Sigma
C	59.03	0.58
O	40.41	0.57
Cl	0.05	0.01
Si	0.16	0.02
K	0.27	0.02
Ca	0.07	0.01
Total	100	
Element	Wt%	Wt% Sigma
C	47.46	1.89
O	34.91	1.42
N	13.13	2.45
Si	0.72	0.05
S	3.02	0.13
K	0.2	0.03
Ca	0.56	0.05
Total	100	
Element	Wt%	Wt% Sigma
C	53.013	0.64
O	45.13	0.64
Si	0.53	0.04
S	0.4	0.04
Co	0.81	0.08
Total	100	

active sites which provided the binding sites for metal ions [35]. UPG shows the removal efficiency 34.85% to 57.82% when amount of biosorbent increased from 0.1 g/50 mL to 1 g/50 mL while this trend was steeper in case of modified plant biomass as the removal efficiency increased to 78.98% when 1 g/50 mL biosorbent was used.

### 3.3. Effect of pH

Biosorption process is affected by initial pH as this parameter has impact factor on solution chemistry, surface charge, degree of ionization and metal ion behavior [36,37]. Nature and behavior of metal ions for biosorption change with the change in pH. MPG and UPG showed maximum biosorption at pH = 6. At low pH, functional groups are protonated and showed positive charge which showed no attraction for the divalent metal ions for attachment as the result biosorption is quiet low, as shown in Fig. 4 [38,39]. With the increase in pH deprotonation occurred, removal of H<sup>+</sup> favored the negative charge which had a great attraction for divalent positive metal ions until optimum pH was obtained i.e. 6. At high pH, solution became alkaline and metal ions had the tendency to precipitate in the form of hydroxide in spite of removal from aqueous solution by biosorption on plant biomass. Similar trend is observed by other divalent metal cations [40,41]. Although maximum biosorption is shown at same pH but it is clearly indicated

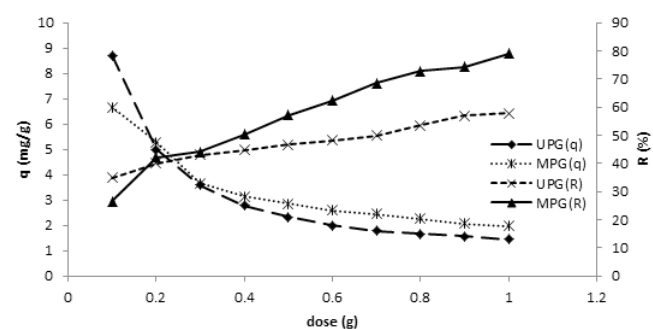


Fig. 3 Effect of *Pennisetum glaucum* dose on removal of Co<sup>2+</sup> and biosorption capacity (Solution concentration (50 mg/L); contact time (30 mins)).

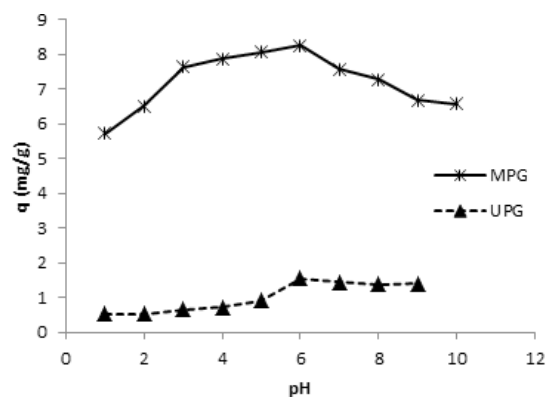


Fig. 4. Effect of pH on Co(II) biosorption by *Pennisetum glaucum*. Solution concentration (50 mg/L); biosorbent dosage (1 g/50 mL for UPG and 0.3 mg/L for MPG); contact time (30 min).



in Fig. 4 that biosorption capacity of modified material is significantly higher than unmodified material. Thiourea actually added active sulphur containing functional group on the surface of biomass which offered better chelation resulting in better biosorption [42].

### 3.4. Biosorption kinetics-effect of time

Biosorption kinetics is studied with the help of study of time factor as it is the promising factor for the determination of rate of biosorption process. Plot of biosorption capacity and time indicated the minimum time required for the attainment of equilibrium which is 5 min for MPG and 20 min for UPG. This equilibrium is between the solid biosorbent and metal ions in aqueous solution and after equilibrium a straight line parallel to x axis is obtained in the plot as shown in Fig. 5. It is clearly indicated that MPG attained equilibrium more rapidly as compared to UPG so it can be inferred that modified material is enriched with the functional groups which are more prone to the attachment of metal ions from the solution. More active surface area is available for small size particle so rate of reaction increases and equilibrium is obtained rapidly [43]. More rapidly Co (II) attached with the functional groups more readily equilibrium was obtained. Once equilibrium is established it became difficult for Co metal ions to find the vacant active sites for attachment and desorption process continued side wise. Initially all active sites were available so process was fast but with passage of time it became difficult for metal ions to find the attachment site [44]. Time for the attainment of equilibrium is almost same for UPG and MPG but value of biosorption capacity for modified biomass is significantly higher as indicated by Fig. 5 which

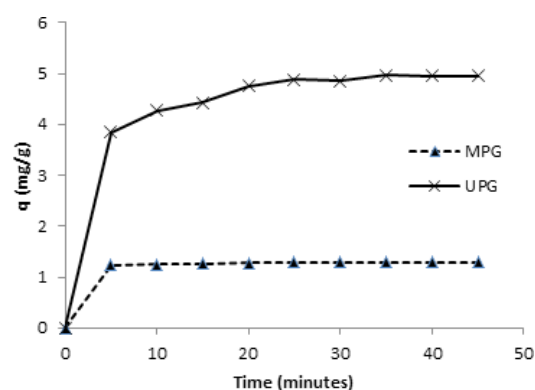


Fig. 5. Effect of contact time on Co (II) biosorption by *Pennisetum glaucum*. Solution concentration (50 mg/L); biosorbent dosage (1 g/50 mL for UPG and 0.5 mg/L for MPG).

supported that thiourea modification enhanced the metal removal capability of biosorbent.

Biosorption kinetics is illustrated well by using two kinetics models and their suitability was determined on the basis of  $R^2$  value and evaluation of experimental and calculated  $q_e$  values. Linear form of pseudo first order (PFO, 4a) and pseudo second order (PSO, 4b) are given as under

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4a)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + t / q_e \quad (4b)$$

where  $q_e$ (mg/g) and  $q_t$ (mg/g) are the uptake capacities of *Pennisetum glaucum* at equilibrium and at instantaneous time  $t$ , respectively.  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{mg/g}\cdot\text{min}$ ) are the pseudo first and second order constants.

PFO parameters are shown in Table 3. Value of  $R^2$  for UPG is 0.92 and for MPG is 0.96 which indicated that it is not reliable model for study of kinetics. Difference between experimental and calculated  $q_e$  is also significant as shown in Table 3 which inferred the non-reliability of this model. The result indicated that number of free active sites is not only factor which is responsible for the rate of biosorption process but there are other factors which must be explained for the rate of reaction.

PSO determines that the rate of reaction depends on the square of number of active sites and metal ion concentration. Value of  $R^2$  for UPG is 0.991 and for MPG is 0.990 which supported the goodness to PSO. Moreover close agreement of calculated and experimental  $q_e$  value indicated that Co (II) biosorption process followed pseudo second order kinetics. As Co(II) is divalent ion so one metal ion occupied two monovalent binding site at a time so rate of biosorption reaction depends on square of active binding sites [45].

### 3.5. The equilibrium modeling with isothermal models

Initial concentrations of metal ions were varied in order to get the comprehensive understanding of interaction of biosorbent and metal ions in solution as biosorption is the accretion of metal ions at interface of two phases. Adsorption isotherm describes the equilibrium relation of these two phases (solid or liquid or solid or gas) of biosorbent and sorbate. This indicates the distribution of particles between these phases while attaining the equilibrium status. Nonlinear approach was employed for Langmuir, Freundlich, Dubinin-Radushkevich (DR) and Temkin models. The mathematical equations for these models are given as under, respectively.

Table 3

Kinetic parameters for the biosorption of  $\text{Co}^{+2}$  on *Pennisetum glaucum*

Adsorbents	Pseudo first order model (PFO)			$q_e$ (exp) (mg/g)	Pseudo second order model (PSO)		
	$k_1$ $\text{min}^{-1}$	$q_e$ (cal) mg/g	$R^2$		$k_2$ (mg/g $\cdot$ min)	$q_e$ (cal) (mg/g)	$R^2$
UPG	0.129	0.15	0.92	1.29	2.136	1.30	0.999
MPG	0.124	2.46	0.96	4.97	0.146	5.16	0.999

$$q_e = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e} \quad (5a)$$

$$q_e = K_f \cdot C_e^{1/n} \quad (5b)$$

$$q_e = q_m \cdot \exp(-\beta \epsilon^2) \quad (5c)$$

$$q_e = B_T \ln K_T \cdot C_e \quad (5d)$$

where  $b$ ,  $K_f$ ,  $1/n$ ,  $\beta$  and  $\epsilon$  are constants. Results obtained from these models were compared and accuracy of the experimental values is judged under RMSE and separation constant factor ( $R_L$ ) is calculated using Eq. (6).

$$R_L = \frac{1}{1 + bC_i} \quad (6)$$

Nature of isothermal reaction is described by  $R_L$ .  $C_i$  is the initial concentration and  $K_L$  is Langmuir constant. If the value is 0 it indicates the irreversible nature of reaction, if value is between 0 and 1 it indicates the favorable nature of reaction while value equal to 1 indicates the linear nature of reaction.

Surface of biosorbent may exhibit different behavior; if biosorption occurs on selective homogenous sites in monolayer pattern then it is studied well under Langmuir isotherm. Langmuir parameters are given in Table 4 which ensured the goodness to fit and experimental data was found covenant with the model. MPG showed greater

Table 4  
Equilibrium modeling of binding of Co by UPG and MPG in batch biosorption process

Langmuir parameters				
Adsorbents	RMSE	$q_{max}$ (mg/g)	$b$ (dm <sup>3</sup> /mg)	$R_L$
UPG	0.19	6.18	0.06	0.085–0.454
MPG	0.42	36.63	0.007	0.442–0.877
Freundlich parameters				
		$K_f$ (mg/g)/(mg/L)	$N$	
UPG	0.13	0.53	1.65	
MPG	1.79	0.42	2.75	
Temkin parameters				
		$K_T$ (dm <sup>3</sup> /mg)	$B_T$ (kJ/mol)	
UPG	0.16	0.48	1.64	
MPG	1.79	0.15	4.83	
Dubinin-Radushkevich parameters				
		$q_m$ (mg/g)	$\beta$ (mol <sup>2</sup> /J <sup>2</sup> )	(kJ/mol)
UPG	0.57	3.97	0.000002	0.5
MPG	1.11	7.37	0.00001	0.23

biosorption capacity  $q_{max} = 36.63$  mg/g which is significantly greater than UPG biosorption capacity  $q_{max} = 6.18$  mg/g. Modification enhanced the monolayer biosorption potential of plant biomass. Comparison of biosorption capacity of UPG and MPG with other materials is given in Table 6. Favorability of biosorption process is further supported by separation constant factor ( $R_L$ ) which is dimensionless constant and compared by 1. As the value of  $R_L$  is less than 1 both for UPG and MPG for all the initial concentrations so it can be inferred that biosorption process is favorable for this biomass.

Freundlich isothermal model employed the attachment of metal ion on heterogeneous surface in multilayer fashion [46]. Non-linear form is shown in Fig. 7. Feasibility and intensity of binding of Co (II) on the surface is indicated by the value of  $n$  which is 1.65 and 2.75 UPG and MPG respectively. Value of  $n$  for UPG is in the range of 1–2 which indicated the good biosorption as the value increased from 2 as in case of MPG biosorption character became better.

D-R (Dubinin-Radushkevich) model provides over-all information regarding the porosity of the biosorbent surface. The parameters of this model are elaborated in Table 4. Nature of sorption process is evaluated by the value of  $E$  (kJ/mol). Value of  $E$  is less than 16 kJ/mol for the UPG and MPG which indicated the weak metal and biosorbent interaction. Value of  $E$  for UPG is 0.5 kJ/mol and for MPG is 0.23 kJ/mol; this favors physiosorption but not chemisorption.

Temkin model describes the behavior of molecules during biosorption process regarding the distribution of their binding energies. Temkin model supports the linearly decreasing trend of energies. Heat of biosorption ( $B_T$ ) is less than 8 kJ/mol for both UPG and MPG which supported the weak physical interaction of biomass with Co (II). As the value of  $B_T$  is greater for MPG as compared to UPG (as shown in Table 4) so the strength of forces between Co (II) and MPG is greater than the forces between metal ions and UPG.

### 3.6. Thermodynamic studies

Changes in temperature of the solution bring the considerable changes in the biosorption process. These changes

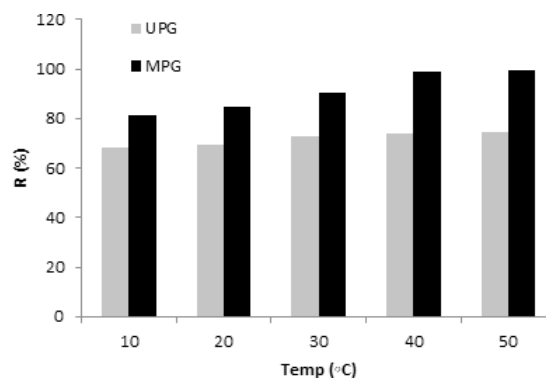


Fig. 6. Effect of temperature on biosorption of Co (II) UPG and MPG. Solution concentration (50 mg/L); biosorbent dosage (1 g/50 mL for UPG and 0.5 mg/L for MPG); contact time (30 min); pH 6.

Table 5  
Thermodynamic parameters for biosorption Co (II) on UPG and MPG

Adsorbent	$\Delta G$ (kJ/mol)			$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol K)
	30°	40°	50°		
UPG	-9.063	-9.389	-9.711	1.723	0.035
MPG	-11.36	-11.964	-12.356	4.293	0.051

Table 6  
Comparison of biosorption capacity of UPG and MPG with other materials

Biosorbent	$q_{max}$ (mg/g)	References
Kaolinite	0.919	[20]
Black carrot residue	5.35	[50]
Arca shell biomass	11.53	[51]
Coir pith	12.82	[52]
Lemon peels	22	[53]
Magnetic Chitosan	27.4	[54]
Almond green hull	45.5	[55]
UPG	6.18	Present study
MPG	36.63	Present study

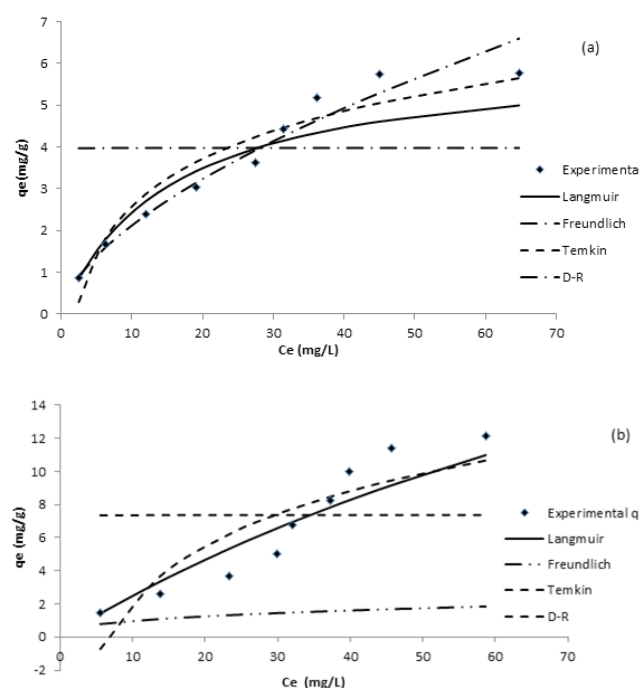


Fig. 7. Nonlinear isotherms plot for  $Co^{+2}$  showing Langmuir, Freundlich, Temkin and DR models by UPG (a) and MPG (b).

affect the temperature dependent factors (enthalpy change ( $\Delta H$ ), free energy change ( $\Delta G$ ) and entropy changes ( $\Delta S$ )) which are calculated by using the equations given below:

$$\Delta G = -RT \ln K_D \quad (7a)$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7b)$$

$$K_D = \frac{C_o - C_e}{C_e} \quad (7c)$$

$\Delta G$  (kJ/mol) is change in Gibbs free energy, T is temperature (K), R is universal gas constant (8.3143 J/mol K) and  $K_D$  is biosorption equilibrium constant derived from Eq. (7c).  $\Delta S$  and  $\Delta H$  was calculated from the intercept and slope respectively by using Eq. (7b).

MPG showed the better percentage recovery of Co metal ions at various temperatures as compared to UPG as shown in Fig. 6. Thermodynamic functions were analyzed by changing the temperature of the solution from 30°C to

50°C as shown in Table 5. Change in temperature brings the observable changes in biosorption process [47]. Biosorption increases with the increase in temperature this is either due to exposure of more active binding sites or due to more diffusion of metal ions on the surface of biosorbent.  $\Delta G$  (kJ/mol) values varied from -9.06 to -9.7 for UPG and -11.36 to -12.35 for MPG which indicated the spontaneity of the process as the values are negative for both materials [48,49].  $\Delta H$  (kJ/mol) values are 1.723 and 4.29 for UPG and MPG respectively which supported the endothermic nature of the process and positive value of enthalpy changes indicated that the process was endothermic in nature. This corresponds to the correct experimental findings. Entropy ( $\Delta S$ ) also supported the stability of binding with MPG as greater the value of entropy greater will be the randomness.

#### 4. Conclusion

Finding of this study concluded that the thiourea modification enhanced the biosorption capacity of *Pennisetum glaucum*. Thiourea enriched the biomass with oxygen, sulphur and nitrogen which added active functionality in it. Biosorption capacity was increased from 6.18 to 36.63 mg/g due to modification of biomass. Optimum pH was found to be 6 and biosorption capacity increased with the increase in temperature. Enthalpy change ( $\Delta H$ ) was observed in range 1.723 to 4.29 kJ/mol with modification and supported the biosorption process. Morphological changes in the biosorbent are due to modifying agent is supportive in the sequestration of toxic metal ions from aqueous solution. In the developing countries like Pakistan where waste water pollution and clean surface water crises are major issues; modification of cheap and abundant biomass might be an acceptable solution.

#### List of symbols

$q_e$	—	Biosorption capacity
$C_i$	—	Initial metal ion concentration
$C_e$	—	Metal ion concentration at equilibrium
$q_e^{(cal)}$	—	Calculated experimental uptake capacity
$q_e^{(exp)}$	—	Experimental uptake capacity
$k_1$	—	pseudo first order constants.

$k_2$	— Pseudo second order constants
$b$	— Langmuir constant
$R_L$	— Separation factor
$K_f$	— Freundlich constant
$n$	— Adsorption intensity
$B$	— Dubinin-Radushkevich (DR) constant
$K_T$	— Temkin constant
$E$	— Dubinin-Radushkevich (DR) constant
$B_T$	— Heat of biosorption
$\Delta H^\circ$	— Enthalpy change
$\Delta G^\circ$	— Free energy change
$\Delta S^\circ$	— Entropy changes
$R$	— Universal gas constant
$K_D$	— Biosorption equilibrium constant

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