

Short communication

## Kinetic studies for Ni(II) biosorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass

Muhammad Asif Hanif<sup>a</sup>, Raziya Nadeem<sup>a</sup>, Muhammad Nadeem Zafar<sup>a</sup>,  
Kalsoom Akhtar<sup>b</sup>, Haq Nawaz Bhatti<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan

<sup>b</sup> Bioprocess Technology Division, National Institute for Biotechnology and Genetic Engineering (NIBGE), Faisalabad 577, Pakistan

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### Abstract

The present study explores the ability of *Cassia fistula* waste biomass to remove Ni(II) from industrial effluents. *C. fistula* biomass was found very effective for Ni(II) removal from wastewater of Ghee Industry (GI), Nickel Chrome Plating Industry (Ni–Cr PI), Battery Manufacturing Industry (BMI), Tanner Industry: Lower Heat Unit (TILHU), Tannery Industry: Higher Heat Unit (TIHHU), Textile Industry: Dying Unit (TIDU) and Textile Industry: Finishing Unit (TIFU). The initial Ni(II) concentration in industrial effluents was found to be  $34.89 \pm 0.01$ ,  $183.56 \pm 0.08$ ,  $21.19 \pm 0.01$ ,  $43.29 \pm 0.03$ ,  $47.26 \pm 0.02$ ,  $31.38 \pm 0.01$  and  $31.09 \pm 0.01$  mg/L in GI, Ni–Cr PI, BMI, TILHU, TIHHU, TIDU and TIFU, respectively. After biosorption the final Ni(II) concentration in industrial effluents was found to be  $0.05 \pm 0.01$ ,  $17.26 \pm 0.08$ ,  $0.03 \pm 0.01$ ,  $0.05 \pm 0.01$ ,  $0.1 \pm 0.01$ ,  $0.07 \pm 0.01$  and  $0.06 \pm 0.01$  mg/L in GI, Ni–Cr PI, BMI, TILHU, TIHHU, TIDU and TIFU, respectively. The % sorption Ni(II) ability of *C. fistula* from seven industries included in present study tend to be in following order: TILHU (99.88) > GI (99.85)  $\approx$  BMI (99.85) > TIFU (99.80) > TIHHU (99.78) > TIDU (99.77)  $\gg$  Ni–Cr PI (90.59). Sorption kinetic experiments were performed in order to investigate proper sorption time for Ni(II) removal from wastewater. Batch metal ion uptake capacity experiments indicated that sorption equilibrium reached much faster in case of industrial wastewater samples (480 min) in comparison to synthetic wastewater (1440 min) using same biosorbent. The kinetic data were analyzed in term of pseudo-first-order and pseudo-second-order expressions. Pseudo-second-order model described well the sorption kinetics of Ni(II) onto *C. fistula* biomass from industrial effluents in comparison to pseudo-first-order kinetic model. Due to unique high Ni(II) sorption capacity of *C. fistula* waste biomass it can be concluded that it is an excellent biosorbent for Ni(II) uptake from industrial effluents.

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**Keywords:** *Cassia fistula*; Biosorption; Wastewater; Ni(II); Industries; Pollution

### 1. Introduction

Removal of Ni(II) from industrial effluents is of primary importance, because contamination of wastewater by it is a very serious health and environmental problem. Ni(II) and its various compounds are extensively being used in various industries. Since the toxic Ni(II) ions dissolve in water, so they can eventually reach the top of the food chain and thus become a risk factor for people's health. Electroplating, dyeing, printing, tanning and ghee manufacturing sectors, are the largest chemical waste producers in the world. Wastewater generated

by these industries often contains high concentration of Ni(II) ions [1]. Effluent treatment processes are designed to ensure that when wastewaters are discharged into natural water courses, any adverse effect are reduced or prevented [2]. Therefore, several technologies for treating heavy metal bearing wastewater, such as precipitation [3,4], reduction [5], solvent extraction [6–8] and membrane processes [9–11] have been used until recently. However, these methods have several disadvantages; which include incomplete metal removal and toxic sludge generation. On the other hand, the use of artificially prepared ion exchange resins is effective, but too expensive to be applied on industrial scale. For this reason, the potential of a new method of removing heavy metals by biological biosorbents presents an important break through [12–16]. Several studies have shown that non-living plant biomass materials are effective for the removal of

\* Corresponding author.

E-mail address: [hnbhatti2005@yahoo.com](mailto:hnbhatti2005@yahoo.com) (H.N. Bhatti).

trace metals from environment [12,14,17–19]. *Cassia fistula* is very popular ornamental tree all around the world. *C. fistula* is commonly known as Amaltas in Pakistan, as Indian Labrum in India, Canafistula in Brazil and as Golden Shower world wide. It belongs to family: Fabaceae, genus: Cassia, Species: Fistula. Numerous ionizable chemical groups have been suggested to responsible for metal biosorption [20]. *C. fistula* presents a high content of ionizable groups such as carboxyl, carbonyl, alcoholic and amino groups specifically and has been previously identified as a very promising biosorbent to remove Ni(II) from synthetic aqueous solutions [14]. Before selecting a wastewater treatment system, a considerable amount of laboratory work must be completed. Testability studies should be conducted to confirm that the process will satisfy effluent standards, the type of chemical or sorbent/membrane envisaged is applicable to the specific waste stream [2,20]. The objective of present study was to access the ability of *C. fistula* waste biomass to remove Ni(II) from industrial effluents.

## 2. Materials and methods

### 2.1. Reagents

All reagents used in present study were of analytical grade. Conc. HNO<sub>3</sub>, Conc. HCl and NaOH were obtained from Merck while Ni(II) atomic absorption spectrometer standard solution (1000 mg/L) was purchased from Fluka chemicals. All glassware and polypropylene flasks used were overnight immersed in 10% (v/v) HNO<sub>3</sub> and rinsed several times with distilled deionized water (DDW). For adjusting the pH of the medium 0.1N solutions of NaOH and HCl were used.

### 2.2. *C. fistula* biomass

*C. fistula* biomass used in present study was harvested from University of Agriculture, Faisalabad, Pakistan by manually removing the matured pods from plants. Biomass was washed thoroughly with DDW to remove any debris and particulate matter. The air dried pods were cut into 5 cm and carefully placed in a built in purring edge peeler of multi purpose wonder mill to obtain the *C. fistula* pods bark. Thus obtained pods bark was oven dried at 60 °C for 72 h until the constant weight. The dried biomass was cut, ground using food processor (Moulinex, France) and then sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain biosorbent with homogenous known particle size of <0.255 mm. No other chemical and/or physical treatments were used prior to biosorption experiments. The selection of this biosorbent for present study was based on its easy availability, cheapness and earlier studies in our laboratory in which this biomass was found very effective in removing Ni(II) from synthetic wastewater [14].

### 2.3. Industrial effluents collection

The wastewater samples from seven industries including Ghee Industry (GI), Nickel Chrome Plating Industry (Ni–Cr PI), Battery Manufacturing Industry (BMI), Tannery Industry:

Lower Heat Unit (TILHU), Tannery Industry: Higher Heat Unit (TIHHU), Textile Industry: Dyeing Unit (TIDU) and Textile Industry: Finishing Unit (TIFU) was collected from city zone of Faisalabad, Pakistan. Triplicate samples were collected in polyethylene bottles and placed in a cooler for transportation to research laboratory [21]. The physiochemical parameters of collected effluents were determined and were presented in one of our earlier work [22].

### 2.4. Batch biosorption studies

The affinity of *C. fistula* biomass to adsorb Ni(II) ions was studied in triplicate sets of experiments. In all sets of experiments fixed volume of industrial effluents containing Ni(II) (200 mL) of pH 6 was thoroughly mixed (at 100 rpm on an orbital shaker) with optimized amount of biosorbent dose (0.1 g/100 mL) of particle size <0.255 mm for predetermined time interval (15–1440 min) at 30 °C. The selection of these parameters for Ni(II) biosorption by *C. fistula* biomass was based on earlier experimental studies [14]. A control assay was also run under similar conditions with the effluent samples. At the end of experiments, the flasks were removed from the shaker and the solution was separated from biomass through filter paper (Whatman No. 40, ashless).

### 2.5. Determination of Ni(II) contents in the solutions

Ni(II) contents in sample and control assays were analyzed using Perkin-Elmer Analyst 300 atomic absorption spectrophotometer equipped with an air acetylene burner and controlled by Intel Pentium-4 personal computer. The analytical wavelength was set at 232 nm and hollow cathode lamp was operated at 25 mA.

### 2.6. Calculations

The metal concentration in the liquid phase was determined at beginning ( $C_i$ ) and equilibration ( $C_e$ ). The following equations were used to compute the percent metal uptake by the sorbent (Eq. (1)) and sorbent uptake capacity at equilibrium  $q_e$  (mg/g) (Eq. (2)).

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

$$q_e = (C_i - C_e) \times \frac{V}{1000w} \quad (2)$$

where  $V$  is the volume of solution in mL and  $w$  is the mass of sorbent in g.

Average and standard deviation values from triplicates were calculated using Microsoft Excel 2004, version Office XP, software. The error bars shown in Fig. 1 represents the standard deviation values. The correlation coefficient ( $R^2$ ) values of the linear form of pseudo-first-order and pseudo-second-order models were also determined using statistical functions of Microsoft Excel, 2004 (version Office XP, Microsoft Corporation, USA).

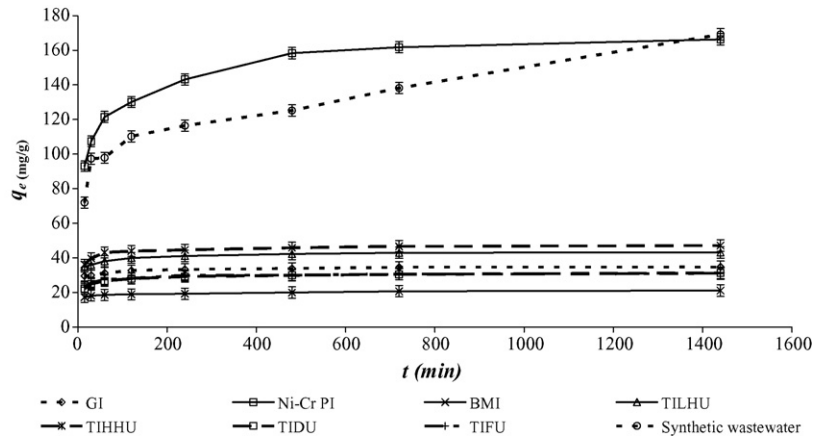


Fig. 1. Sorption kinetics plot for Ni(II) removal by *Cassia fistula* biomass from industrial and synthetic wastewater.

### 3. Results and discussion

Kinetic information of metal uptake by biosorbent is required for selecting optimum operating conditions for industrial scale batch metal removal process [23,24]. Initial and equilibrium concentrations of Ni(II) in industrial wastewater used for kinetic experiments are tabulated in Table 1. The solution pH was kept constant at 6 during metal biosorption by biosorbent. The sorption kinetic plot of Ni(II) from industrial effluents is presented in Fig. 1. From Fig. 1 it is obvious that the sorption equilibrium for Ni(II) was achieved within 480 min in case of industrial effluents, in comparison to 1440 min sorption equilibrium for synthetic wastewater [14]. This variation was due to the presence of co-metal ions in case of industrial effluents which were absent in case of synthetic wastewater. Due to presence of greater number of metal ions in industrial wastewater, the sorption equilibrium was reached much faster due to faster occupancy of sorption sites by metal ions [22]. Ni(II) biosorption was faster in first hour of contact, followed by slow biosorption till equilibrium was achieved. This variation in biosorption behaviour was also reported previously [25,26]. Mathematical models that can describe the behaviour of a batch biosorption process under different experimental condition are useful for scale up studies or process optimization. Pseudo-first-order and pseudo-second-order kinetic models have been extensively used to describe the kinetics of metal biosorption in batch systems [27–30]. The finally selected model will be that, which not only fit closely the data, but also explain responsible sorption mechanisms. In this study *C. fistula* biomass was employed as free cell suspension in a well agitated batch system, where all the cell wall binding sites were readily available for Ni(II) uptake, hence the

effect of external film diffusion on biosorption rate can safely assumed as less significant and can be ignored in kinetic modeling. Both pseudo-first-order and pseudo-second-order kinetic models were used for the evaluation of the experimental data of Ni(II) biosorption by *C. fistula* biomass. Most commonly used pseudo-first-order Lagrengren model is generally expressed as (Eq. (3)) [27]:

$$\frac{dq}{dt} = k_{1,ads}(q_e - q) \quad (3)$$

where  $q_e$  (mg/g) and  $q$  (mg/g) are amounts of adsorbed metal ions on the biosorbent at sorption equilibrium between two phases (solid and liquid phases) and at any time  $t$ , respectively; and  $k_{1,ads}$  is the Lagrengren rate constant. Linearized form of Lagrengren model can be obtained on integrating Eq. (3) between limits of,  $t=0$  to  $t=t$  and  $q=0$  to  $q=q_e$ , it becomes (Eq. (4))

$$\log(q_e - q) = \log q_e - k_{1,ads} \frac{t}{2.303} \quad (4)$$

Linear plot of  $\log(q_e - q)$  versus  $t$  having high value of coefficient of determination ( $R^2$ ) indicates the applicability of this kinetic model. The main assumption of pseudo-second-order kinetic model is that biosorption follows second-order mechanism. So, the rate of loading of biosorption sites with metal ions is proportional to the square of number of free sites (Eq. (5)):

$$\frac{dq}{dt} = k_{2,ads}(q_e - q)^2 \quad (5)$$

where  $k_{2,ads}$  (g/mg min) is rate constant of pseudo-second-order kinetic model. On integrating Eq. (5) between limits of  $t=0$

Table 1  
Initial and equilibrium concentrations of Ni(II) in industrial wastewater collected from city zone of Faisalabad, Pakistan

	Site						
	GI (mg/L)	Ni-Cr PI (mg/L)	BMI (mg/L)	TILHU (mg/L)	TIHHU (mg/L)	TIDU (mg/L)	TIFU (mg/L)
$C_i$	34.89 ± 0.01	183.56 ± 0.08	21.19 ± 0.01	43.29 ± 0.03	47.26 ± 0.02	31.38 ± 0.01	31.09 ± 0.01
$C_e$	0.05 ± 0.01	17.26 ± 0.08	0.03 ± 0.01	0.05 ± 0.01	0.1 ± 0.01	0.07 ± 0.01	0.06 ± 0.01
% sorption	99.85	90.59	99.85	99.88	99.78	99.77	99.80

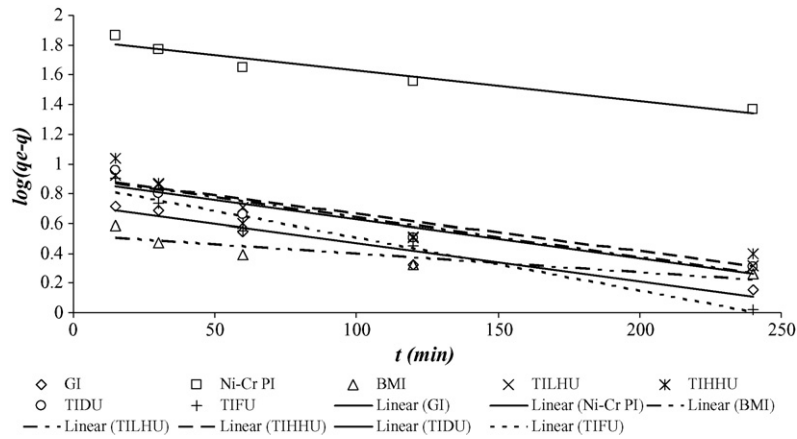


Fig. 2. Lagergren pseudo-first-order sorption kinetics plot of Ni(II) biosorption from industrial wastewater onto *C. fistula* biomass.

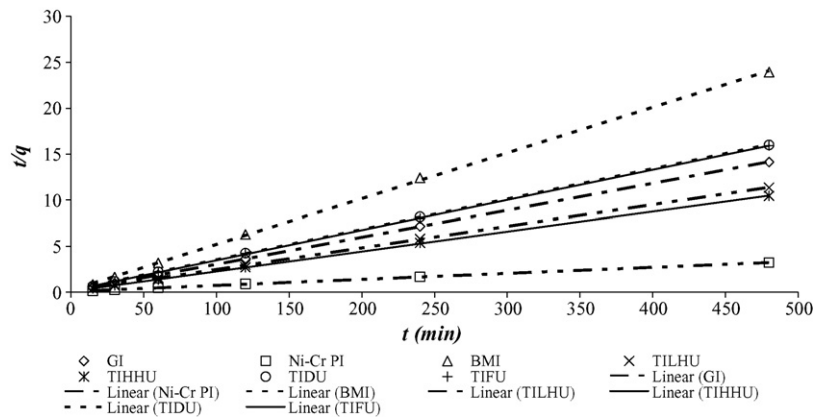


Fig. 3. Pseudo-second-order sorption kinetics plot of Ni(II) biosorption from industrial wastewater onto *C. fistula* biomass.

Table 2  
Comparison between adsorption parameters of Lagergren pseudo-first-order and pseudo-second-order kinetic models

Site	Pseudo-first-order kinetic model			Experimental value, $q_e$ (mg/g)	Pseudo-second-order kinetic model		
	$q_e$ (mg/g)	$K_{1,ads}$ ( $\times 10^{-4} \text{ min}^{-1}$ )	$R^2$		$q_e$ (mg/g)	$K_{2,ads}$ (g/mg min)	$R^2$
GI	4.49	6.94	0.8937	34.84	34.24	$6.58 \times 10^{-3}$	0.9999
Ni–Cr PI	58.89	5.21	0.8615	166.3	151.51	$4.69 \times 10^{-3}$	0.9996
BMI	3.18	4.34	0.9079	21.16	20.16	$1.02 \times 10^{-3}$	0.9997
TILHU	7.19	8.68	0.9439	43.24	42.73	$3.75 \times 10^{-2}$	0.9999
TIHHU	7.14	7.38	0.8226	47.16	46.26	$4.10 \times 10^{-3}$	0.9999
TIDU	6.56	6.94	0.8688	31.31	30.39	$4.32 \times 10^{-3}$	0.9999
TIFU	5.52	8.68	0.8236	31.03	30.58	$5.08 \times 10^{-3}$	0.9999

to  $t=t$  and  $q=0$  to  $q=q_e$ , linearized form of model can be represented as (Eq. (6)):

$$\frac{t}{q} = \frac{1}{k_{2,ads}} q_e^2 - \frac{t}{q_e} \quad (6)$$

The sorption data of Ni(II) uptake by *C. fistula* biomass fitted with pseudo-first-order and pseudo-second-order kinetic model is shown in Figs. 2 and 3, respectively and the obtained models parameters are tabulated in Table 2. It is clear from Table 2 that coefficient of correlation ( $R^2$ ) for the pseudo-second-order kinetic model is much higher in case of all industrial effluents in comparison to pseudo-first-order model. The other fact that is noted from the same table is the close agreement between the

estimated  $q_e$  (mg/g) values and experimental  $q_e$  (mg/g) values. Both these observations suggested that the Ni(II) sorption by *C. fistula* pods biomass followed well the pseudo-second-order kinetic model in all cases, which relies on the assumption that biosorption may be the rate limiting step.

#### 4. Conclusions

The following conclusions were drawn from the present study:

- *C. fistula* biomass can be used for removal of Ni(II) from industrial streams very effectively.

- The obtained results strongly demonstrated that metal – biosorbent sorption equilibrium was much faster in case of industrial effluents in comparison to synthetic effluents.
- Batch metal ion uptake capacity tests have shown that the biosorption process can be better described by pseudo-second-order kinetic model.

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