RESEARCH ARTICLE

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Nickel removal by biosorption onto medlar male flowers coupled with photocatalysis on the spinel ZnMn_2O_4

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Abstract

Ni^{2+} is a highly toxic above 0.07 mg/L and its removal is of high significance. The biosorption of Ni^{2+} onto medlar male flowers (MMF) was studied in relation with the physical parameters like pH, contact time, biosorbent dosage, Ni^{2+} concentration and temperature. The interaction biosorbent- Ni^{2+} was examined by the FTIR technique. The equilibrium was achieved within 40 min and the data were well fitted by the Langmuir and Redlich-Peterson (R-P) models. The maximum Ni^{2+} uptake capacity was 17.073 mg/g at 25°C and the Ni^{2+} removal follows a pseudo-second order kinetic with activation energy of 13.3 kJ/mol. The thermodynamic parameters: ΔS° , ΔH° and ΔG° showed that the biosorption was spontaneous and endothermic. MMF was used as a post treatment technique and the biosorption was coupled with the visible light driven Ni^{2+} reduction over the spinel ZnMn_2O_4 . The effect of the pH, ZnMn_2O_4 loading and light intensity on the photoactivity was investigated. 77.5% of Ni^{2+} was reduced after ~140 min under optimal conditions. The Ni^{2+} removal reached a rate conversion of 96% of with the coupled system biosorption/photocatalysis is very promising for the water treatment.

Keywords: Biosorption, Nickel, Medlar male flower, Photocatalytic

Introduction

Extensive industrial activities have led to tremendous increase in the use of toxic metals over the last decades provoking large scale pollution. Soil and water were continuously contaminated by heavy metals coming from various industries. Ni^{2+} cannot be biodegraded unlike organic pollutants; it persists indefinitely and accumulates through the food chain, thus posing a serious threat to human health [1]. Nickel is known as one of the most common toxic metals and inhaled nickel compounds are carcinogenic and provoke asthma, chronic bronchitis, pulmonary embolism as well as respiratory and may bring nausea, dizziness and diarrhea [2,3]. The WHO has drastically reduced at 0.07 mg/L the authorized threshold for nickel in drinking water [4]. Therefore, it was necessary to treat metal-contaminated water prior its discharge in the aquatic environment. Several techniques

have been used to this end, like precipitation, ion exchange, biosorption and membranes [5]. In recent years, considerable attention has been focused on the biosorption using agricultural materials [6,7]. Hence, efforts were done to develop inexpensive biosorbents using agricultural wastes. We have tested several biological materials for the metals removal and studies were carried out to investigate the potential of locally available biosorbent namely the medlar male flowers (MMF) for the nickel removal from aqueous solutions. The contact time, biosorbent dose, pH, Ni^{2+} concentration and temperature were optimized. To understand the nature of the Ni^{2+} biosorption on MMF, equilibrium isotherms were analyzed by the Freundlich, Langmuir and Redlich-Peterson (R-P) models. Kinetic and thermodynamic parameters were also evaluated.

On the other hand, the biosorption greatly reduces the pollution but often not enough to comply with the standards of the world health organization. At this level, the photocatalysis appears to be quite promising because

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of its simplicity. There were only few studies on the combined systems (biosorption/photocatalysis) for the water treatment. So, in a second step, the system was directed to the spinel photocatalyst ZnMn_2O_4 which was presented as having the required photoelectrochemical parameters. Its conduction band (CB) derives from $3d$ orbital able to reduce metal ions to the elemental states. In addition, it is low cost, non-toxic and chemically stable under the operating conditions.

Experimental

MMF obtained from local farms (Algiers) is thoroughly washed with water and dried at 80°C . Then, it was crushed, ground in an agate mortar and sieved to select a particle size of $500\ \mu\text{m}$ by using an ASTM standard sieve. It was stored in closed bottles until use.

The Ni^{2+} stock solution (1 g/L) was prepared by dissolving the accurate quantity of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Merck, 99%) in distilled water. Concentrations down to 50 mg/L were prepared by dilution. The pH was adjusted to the desired value by addition HCl or NaOH using a digital pH meter (Schott 825). The batch experiments were done in a double walled Pyrex reactor of $500\ \text{cm}^3$ capacity (Figure 1) whose temperature was regulated by a thermostated bath (Julabo) under magnetic stirring (500 rpm). This was achieved to investigate the optimal conditions of pH (2–7), biosorbent dosage (3–9 g/L), Ni^{2+} concentrations (50–250 mg/L) and temperature (15– 55°C). The aliquots were withdrawn at regular time intervals and filtered off. The supernatant was analyzed for residual Ni^{2+} concentration with a double beam UV-Visible spectrophotometer (Shimadzu 1800). The solution was mixed to dimethylglyoxime in presence of bromine in ammoniacal medium and the complex was titrated at 465 nm. The turbidity was measured using an Aqualytic turbidimeter (WTW Turb 550). The amount of

Ni^{2+} uptake and the biosorption percentage were calculated from the relations:

$$q = (C_o - C) \frac{V}{m_s} \quad (1)$$

$$(\%) = \frac{C_o - C}{C_o} \times 100 \quad (2)$$

The FTIR spectra of unloaded and Ni^{2+} loaded MMF were recorded on an infrared spectrometer (Jasco-3200) using the KBr routine technique. The specific surface area was measured by the BET method with a Quadrasorb SI apparatus (Micromeritics ASAP 2010). The point of zero charge (pzc) was determined by the immersion technique described elsewhere [8].

The spinel ZnMn_2O_4 was synthesized by sol-gel. A stoichiometric mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.025 M/0.05 M), both of purity greater than 99%, was dissolved in 60 mL of ethylene glycol at room temperature. The solution was heated under stirring at 70°C (6 h) under reflux and the viscous solution was dried at 120°C . The amorphous powder was heated at 850°C and furnace cooled. The phase was confirmed by X-ray diffraction (XRD) using monochromatized Cu K α radiation. The photocatalytic tests were carried out in the same reactor (Figure 1). The light source was a 200 W tungsten lamp (Osram) disposed at 10 cm above the reactor. The light flux was measured with a commercial light meter (roline RO 1332). The light was turned on after a transition period of 2 h for the dark adsorption onto the spinel.

Results and discussion

Characterization of the biosorbent

The physical characteristics of MMF were summarized in Table 1. The FTIR spectra of unloaded and Ni^{2+} -loaded

Figure 1 A schematic diagram of the coupled biosorption/photocatalysis system.

Table 1 Physico-chemical characterization of the MMF

Parameters	
Particle size (mm)	0.5
BET surface area (m ² /g)	2.78
pH _{PZC}	7.26

MMF (Figure 2) were compared to get insights on the nature of the biosorbent-Ni²⁺ interactions and to determine the frequency changes in the functional groups for Ni²⁺ binding. The spectrum of MMF shows a strong band at 3444 cm⁻¹ attributed to hydroxyl groups. The peak at 2920 cm⁻¹ is due to the C-H stretching frequency whereas that at 1644 cm⁻¹ is assigned to C=O stretching of the primary and secondary amides (NH₂CO). The peaks at 1505 and 1382 cm⁻¹ are due to N-H stretching of primary and secondary amides, and amide (III) respectively. Bands at 1320 and 1243 cm⁻¹ are characteristic of carboxylic acids. The strong C-O band at 1057 cm⁻¹ confirms the lignin structure of MMF [9]. The FTIR spectrum of Ni²⁺ loaded MMF (Figure 2b) shows a decrease in intensity and a shift in asymmetric stretching frequencies at 3444, 1644 and 1505 cm⁻¹ due to coordinated Ni²⁺ ions by hydroxyl, carboxyl, and amides groups respectively on the MMF surface.

Effect of contact time

The effect of the contact time on the rate of Ni²⁺ removal is shown in Figure 3. The process was rapid at the beginning due to large surface area of the biosorbent and gradually decreases to reach an equilibrium state. The plots reveal that the maximum percentage of Ni²⁺ removal occurs after 40 min of shaking. Then, the biosorption becomes controlled by the rate of Ni²⁺ transported to internal sites of the grains.

Effect of the biosorbent dose

As expected, the Ni²⁺ biosorption increases with increasing the MMF dose, and becomes almost constant beyond 7 g/L (Figure 4). With increasing the MMF dose, more surface area is available due to increasing number of active sites, thus making easier the penetration of Ni²⁺ to the biosorption sites. So, we have used a biosorbent dose of 7 g/L for the following experiments. Further increase of the mass does not produce a significant effect on the Ni²⁺ biosorption because of the saturation effect. This new biosorbent could not only remove Ni²⁺, but also produces a weak turbidity not exceeding 1.73 NTU which an acceptable value. It is worthwhile to outline that a low turbidity is an important requirement for the water treatment.

The pH is an important parameter for controlling the biosorption and its influence on the Ni²⁺ uptake by MMF is illustrated in Figure 5. Experiments were done by varying the pH over the range (2–7) at 25°C with

MMF dose of 7 g/L. The performance increases rapidly with increasing pH up to 5, then slowly and beyond pH 8.5, $\text{Ni}(\text{OH})_2$ precipitates owing to the low solubility product ($\sim 10^{-16}$). At acidic pHs, the MMF surface is covered by H^+ ions and Ni^{2+} cannot compete for biosorption sites. The increase in the biosorption at higher pHs is likely associated with deprotonation of the biosorbent surface or other negatively charged groups lead to electrostatic attraction of Ni^{2+} ions. Based on these results, the best biosorption occurs at $\text{pH} \sim 7$ with a percentage removal of 83%. Accordingly, the further biosorption studies are carried around this pH which is close to the real pH of natural medium.

Effect of temperature

The thermal variation of the Ni^{2+} uptake at a concentration of 100 mg/L onto MMF is shown in Figure 6. An increase of the temperature results in an enhanced biosorption rate and the maximum uptake occurs at 40°C.

At that temperature, an increasing number of molecules acquire sufficient energy to interact with active sites. Furthermore, raising temperature produces a swelling effect within the internal MMF structure, thus enabling large amount of Ni^{2+} ions to access to inside cavities.

The Ni^{2+} removal, evaluated for the biosorption isotherms, clearly indicates an endothermic process. However, the biosorption was found to decrease at higher temperatures (55°C) possibly due to the damage of active binding sites in the biomass. In addition, the water vaporization becomes an increasing problem. Nevertheless, the temperature-dependence is somewhat different in our case, and this may be due to the differences in the experimental conditions and the nature of the biosorbent. As a result, the temperature of 40°C is found to be optimal. However, the Ni^{2+} biosorption at 40°C (84%) is close to that at 25°C (82%). So, to save energy the last temperature is selected for further experiments.

Table 2 The isotherm constants for the Ni²⁺ biosorption onto MMF under optimized conditions for Langmuir Freundlich and Redlich-Peterson models

Langmuir			Freundlich			Redlich-Peterson			
q _m	b	R ²	N	K _f	R ²	K _R	a _R	g	R ²
17.143	0.125	0.9984	0.232	5.650	0.9054	1.996	0.104	1.024	0.9990

Effect of initial concentration

Nickel comes from industrial activities and discharged in the aquatic medium at concentration up to 400 mg/L. So it is interesting to study the effect of concentration. The equilibrium Ni²⁺ uptake for different concentrations (50–250 mg/L) at 25°C on MMF (7 g/L) at pH ~ 7 is shown in Figure 7. The biosorption rate decreases with increasing Ni²⁺ concentration from 83% (50 mg/L) to 62% (250 mg/L). At low Ni²⁺ concentrations, the binding sites are unsaturated and consequently available for the biosorption process. By contrast, for high Ni²⁺ concentrations the number of ions competing for the available sites on the biomass increases, thus resulting in a decrease of the Ni²⁺ biosorption.

Biosorption isotherms

The analysis of the isotherm by fitting the experimental data to various models is an important step for the design purpose. Three models are tested namely the Langmuir, Freundlich and Redlich–Peterson (R-P) ones. a) The Langmuir model is successfully used for homogenous biosorption surface [2]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

Figure 8 illustrates the plots at 25°C, the constants q_m and b are gathered in Table 2.

The high coefficients R² show that the Ni²⁺ biosorption onto MMF follows the Langmuir model whose main feature is expressed in term of a dimensionless separation constant (R_L) [10]:

$$R_L = \frac{1}{1 + b C_o} \quad (4)$$

The R_L value indicates the type of isotherm: unfavorable (R_L > 1), linear (R_L = 1), favorable (0 < R_L < 1) or irreversible (R_L = 0) [10]. The R_L values for different Ni²⁺ concentrations are given in Table 3. It can be observed

Table 3 The separation factor versus the initial Ni²⁺ concentration

C _o (mg/L)	40	60	80	100	150	200	250
R _L	0.0868	0.0596	0.0454	0.0366	0.0247	0.0186	0.0150

that R_L lies in the range 0–1 in all experiments, thus confirming the favorable Ni²⁺ uptake onto MMF.

The maximum biosorption capacity (q_m) is compared with other biosorbents reported in the literature (Table 4), where q_m has not been derived specifically. One can see that the maximum Ni²⁺ biosorption capacity is intermediate compared to other biosorbents and MMF is a promising for the water treatment. b) The Freundlich model is suitable for heterogeneous surfaces [11]:

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

Figure 8 shows the plots while the constants K_f and 1/n are given in Table 2. The values of 1/n, less than 1, indicating a favorable biosorption. However, the theoretical values deviate from the experimental data suggesting that the model is not appropriate to describe the Ni²⁺ biosorption onto MMF.

c) The R–P model combines both the Langmuir and Freundlich ones and the hybrid mechanism does not follow a monolayer biosorption [14]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (6)$$

The exponent g varies between 0 and 1. It is helpful to outline that for g = 1, the equation converts simply to the Langmuir isotherm while for g = 0, it is simplified to the Henry's law. For 1 << a_R C_e^g, the model is identical to the Freundlich one. Table 2 lists the biosorption parameters together with the R² values. A comparison between the theoretical and experimental data of Ni²⁺ biosorption onto MMF was well illustrated in Figure 8. The R–P equation applied over the whole concentrations range gives a coefficient R² close to 1, thus

Table 4 Biosorption capacities of different biosorbents for Ni²⁺ removal from water

Biosorbent	q _m (mg/g)	Ref.
Gracilaria caudata	45	[2]
Sargassum muticum	70	[2]
Tea factory waste	15.2	[3]
Activated sludge	238.1	[5]
Baker's yeast	8.2	[12]
Aspergillus niger	4.82	[13]
Medlar male flower	17	This study

Figure 9 Biosorption kinetics plot of Ni^{2+} onto MMF biomass.

confirming the best fit for Ni^{2+} biosorption for the two models. The g values were close to unity and this means that the isotherm approaches the Langmuir model rather than the Freundlich one. Hence, the good fit of the equilibrium data for Langmuir and R-P isotherms confirms the monolayer coverage of Ni^{2+} onto MMF.

Biosorption kinetic

The biosorption kinetic is important from a practical point of view since it controls the efficiency of the process and the models correlate the Ni^{2+} uptake rate with the bulk concentration. In order to analyze the biosorption rate, the kinetic data were modeled with the Lagergren pseudo-first-order and pseudo-second order equations [15].

$$\text{Pseudo-first-order} : q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

$$\text{Pseudo-second-order} : q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \quad (8)$$

where q_t and q_e are the amounts of Ni^{2+} adsorbed (mg/g) at time (t) and at equilibrium, respectively, k_1 (min^{-1}) and k_2 (mg/g min) are the corresponding rate constants. q_b , k_1 , and k_2 were calculated by the non-linear regression analysis (Figure 9) using the Origin program (version 7.5). The optimization uses the error function to fit the experimental data.

The coefficients R^2 and the chi-square test (χ^2) were used to measure the goodness-of-fit:

$$\chi^2 = \sum_{i=1}^N \frac{(q_e - q_i)}{q_i} \quad (9)$$

where q_e is the observation from the batch experiment, q_i the estimate from the isotherm for corresponding q_e and N the number of observations in the experimental isotherm. If the data from the model are similar to the experimental ones, χ^2 is small [16]. The coefficients R^2 and χ^2 in the temperature range (15–55°C) indicate that the biosorption kinetic was well described by the pseudo-second-order equation (Table 5). The comparison of the experimental and theoretical values of q_t evaluated from

Table 5 Kinetic parameters for Ni^{2+} biosorption onto MMF at different temperatures

T (K)	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	χ^2	R^2	k_2 (g/mg min)	$\chi^2 \times 10^3$	R^2
288	0.0634	0.2113	0.9599	0.1327	3.056	0.9880
298	0.1006	0.2711	0.9425	0.1536	0.566	0.9863
313	0.1641	0.1769	0.9315	0.2499	0.762	0.9800
328	0.2169	0.8849	0.9770	0.2987	0.025	0.9938

Table 6 Thermodynamic parameters for the biosorption of Ni²⁺ onto MMF at different temperatures

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
288	-3.460		
298	-3.921	9.806	46.065
313	-4.612		
328	-5.303		

Eq. (8) shows that for all temperatures, q_t is almost constant and increases with temperature along with k_2 .

Thermodynamic parameters of biosorption

The free energy (ΔG°) of the biosorption is related to the equilibrium constant (k_c) by [3]:

$$\Delta G = -RT \ln k_c = \Delta H - T\Delta S, \quad k_c = \frac{C_o - C_e}{C_e} \quad (10)$$

The standard enthalpy (ΔH°) and entropy (ΔS°) were obtained from the linear plot $\ln k_c$ versus $1/T$. The negative value of ΔG° (Table 6) indicates a spontaneous biosorption and the low temperatures make the biosorption easier. The positive values of ΔH° and ΔS° implies that the Ni²⁺ biosorption onto MMF was endothermic with increased randomness at the solid/solution interface.

Photocatalytic process

As mentioned above, the Ni²⁺ uptake on MMF greatly reduces the pollution but not sufficiently to comply with the standards of the water quality. However, the biosorption can be used as post treatment for the photocatalytic process. Using colloidal semiconductor particles as light absorbing units is simple and does not need any sophisticated device. The first step was to generate electron/

hole (e⁻/h⁺) pairs on a semiconductor by energetic photons ($h\nu > E_g$). Ni²⁺ was photo-electrochemically reduced to elemental state. In this respect, the spinel ZnMn₂O₄ shows light absorption for wavelengths shorter than 730 nm. In addition, the oxide is chemically stable and has been elaborated via sol-gel route in order to increase the active surface.

Even though the photocatalytic processes are related to the morphology of the material, a detailed understanding of the fundamental properties is required to get a high-quality powder. ZnMn₂O₄ was synthesized by sol-gel and the XRD pattern (Figure 10) is characteristic of single phase. All peaks are assigned to the spinel phase in agreement with the JCPDS card N° 24-1133. Nevertheless, when the calcination temperature exceeds 850°C, the crystallites can agglomerate in grains and decrease the specific surface area. This has been corroborated by the lack of XRD peak broadening and the relatively small active surface (28 m²/g).

The main interest of this section was to investigate the effect of some physical parameters on the Ni²⁺ photoreduction. A transition period is required before irradiation and the suspension ZnMn₂O₄ was maintained in the dark during this period. The starting concentration was set at 18 ppm and the Ni²⁺ solution was equilibrated with the catalyst during 2 h to establish the adsorption conditions. The difference between the nominal concentration and that of measured after equilibrium was taken as the quantity of adsorbed Ni²⁺ onto ZnMn₂O₄ (~5%). The pH of the solution has a direct influence on the photo-electrodeposition via the surface charge catalyst. With Ni²⁺, the adsorption follows a cationic type law and is pronounced at high pH. We have conducted the experiments for 140 min at different pHs and the

corresponding fractional reduction of Ni²⁺ is presented in Figure 11. It appears that the photoreduction was maximum (~77.5%) at pH 7.5 and decreased rapidly with decreasing pH, in acidic media, the Ni²⁺ were repelled by the positive surface charge of ZnMn₂O₄. In the pH range (3.5-7.5) the photocatalytic Ni²⁺ reduction on ZnMn₂O₄ was rather limited.

The photocatalytic tests were carried out with various amounts of ZnMn₂O₄ and the rate of Ni²⁺ reduction increases with increasing the mass of ZnMn₂O₄ (Figure 12). For smaller doses, less active sites for the reduction process are available and the photoactivity increases in parallel with the amount of ZnMn₂O₄. On the contrary, for higher doses, all photocatalytic sites are saturated and the light scattering of the incident flux, the shadowing effect of the powder catalyst; the metal clusters account for the decrease of the activity.

Indeed, the incident light on the metal surface was partially absorbed and converted to heat. The two opposing effects gave an optimal ZnMn₂O₄ dose of 0.5 g/L. Increasing light intensity enhanced both the rate and the extent of Ni²⁺ reduction (Figure 13).

Taking into account the adsorption and the photoreduction, the modified Langmuir–Hinshelwood model was successfully applied to assess the Ni²⁺ photoreduction rate [17].

$$\frac{-dC}{dt} = k_{app}C_o \quad (11)$$

The reaction occurs between adsorbed species on the spinel surface. The linear plot of $\ln C/C_o$ vs time indicates that the reduction obeys to a first order kinetic

Figure 14 Photoreduction of Ni²⁺ on ZnMn₂O₄. Inset: The plot of $\ln C/C_o$ vs. time.

(Figure 14). The apparent reaction constant (k_{app}) averages 0.42 h^{-1} and the half life, i.e. the time needed for the concentration to fall to half of its initial value, was found to be concentration independent and averages 1.5 h.

Conclusion

An agricultural by product namely the Medlar male flower, locally available has been successfully used for Ni^{2+} biosorption from aqueous solution. The contact time, biosorbent dose, pH and temperature were optimized. The maximum biosorption capacity was obtained at pH 5, and the equilibrium was reached in less than 40 min. The isotherms data were well fitted with both the Langmuir and Redlich-Peterson models. The negative free energy confirmed a favorable Ni^{2+} biosorption where the positive enthalpy indicated an endothermic nature. The spinel ZnMn_2O_4 elaborated by co-precipitation, was used to reduce the remaining concentration by photocatalysis into elemental state. A reduction rate of 77.5% was achieved after 2 h irradiation at pH 7.5 with an optimal ZnMn_2O_4 mass equal to 0.5 g/L. The photoreduction followed a first order kinetic. The results indicated that the coupled system may be a viable alternative and a new way for the Ni^{2+} removal in aquatic medium.

Nomenclature

- b Langmuir biosorption constant (L/mg)
- C_e Residual Ni^{2+} concentration at equilibrium (mg/L)
- C_o Initial Ni^{2+} concentration (mg/L)
- E_g The optical gap
- K_f The Freundlich constants denoting the biosorption capacity ($\text{mg}^{1-1/n}/\text{g L}^{1/n}$)
- k_1 Pseudo-first order biosorption rate constant (min^{-1})
- k_2 Pseudo-second order biosorption rate constant (g/mg min)
- k_{app} The apparent reaction constant
- k_c Standard thermodynamic equilibrium constant.
- k_{app} The apparent reaction constant
- m Biosorbent dosage (g)
- m_s semiconducteur dosage (g)
- n The Freundlich constants denoting the biosorption intensity
- q_e Amount of Ni^{2+} adsorbed on the biosorbent at equilibrium (mg/g)
- q_{max} Langmuir biosorption constant (mg/g)
- q_t Amount of Ni^{2+} adsorbed on the sorbent at any time (mg/g)
- R Universal gas constant
- R^2 Correlation coefficient
- R_L Dimensionless separation factor
- T Absolute temperature (K)
- t Time of biosorption (min)

- ΔG° Free energy (kJ/mol)
- ΔH° Enthalpy change (kJ/mol)
- ΔS° Entropy change (J/mol K)

Competing interests

All authors declare that they have no competing interest.

Authors' contributions

AC and FM were the main authors, designed and performed the study and drafted the manuscript. MT supervised the work. AK helped in the biosorption study. All authors read and approved the final manuscript.

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References

1. Lopez A, Lazaro N, Morales S, Marques AM: Nickel biosorption by free and immobilized cells of *pseudomonas fluorescens* 4F39: a comparative study. *Water Air and Soil Pollutio.* 2002, **135**:157–172(16).
2. Bermúdez YG, Rico ILR, Bermúdez OG, Guibal E: Nickel biosorption using *gracilaria caudata* and *sargassummuticum*. *Chem Eng J* 2011, **166**:122–131.
3. Malkoc E, Nuhoglu Y: Investigations of nickel(II) removal from aqueous solutions using tea factory waste. *J Hazard Mater* 2005, **127**:120–128.
4. WHO: *Nickel in drinking-water. Background document for development of WHO guidelines for drinking-water quality.* 4th edition. Geneva, Switzerland: World Health Organization; 2011.
5. Aksu Z, Aciol U, Kabasakal E, Tezer S: Equilibrium modeling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge. *Water Res* 2002, **36**:3063–3073.
6. Subbiah MV, Vijaya Y, Reddy AS, Yuvaraja G, Krishnaiah A: Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto *trametes versicolor* biomass. *Desalination* 2011, **276**:310–316.
7. Vinodhini V, Das N: Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust. *Desalination* 2010, **264**:9–14.
8. Faria PCC, Órfão JJM, Pereira MFR: Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Res* 2004, **38**:2043–2052.
9. PascoalNeto C, Rocha J, Gil A, Cordeiro N, Esculcas AP, Rocha S, Delgadillo I, Pedrosade Jesus JD, FerrerCorreia AJ: ¹³C solid-state nuclear magnetic resonance and Fourier transform infrared studies of the thermal decomposition of cork. *Solid State Nucl Mag* 1995, **4**:143–151.
10. Ncibi MC, Mahjoub B, Ben Hamissa AM, Ben Mansour R, Seffen M: Biosorption of textile metal-complexed dye from aqueous medium using *posidonia oceanica* (L.) leaf sheaths: mathematical modeling. *Desalination* 2009, **243**:109–121.
11. Chakravarty P, SenSarma N, Sarma HP: Removal of lead(II) from aqueous solution using heartwood of areca catechu powder. *Desalination* 2010, **256**:16–21.
12. Padmavathy V: Biosorption of nickel(II) ions by baker's yeast: Kinetic, thermodynamic and desorption studies. *Bioresour Technol* 2008, **99**:3100–3109.
13. Amini M, Younesi H, Bahramifar N: Biosorption of nickel(II) from aqueous solution by *Aspergillus Niger*: response surface methodology and isotherm study. *Chemosphere* 2009, **75**:1483–1491.
14. Anirudhan TS, Jalajamony S, Suchithra PS: Improved performance of a cellulose-based anion exchanger with tertiary amine functionality for the adsorption of chromium(VI) from aqueous solutions. *Colloids Surf A Physicochem Eng Asp* 2009, **335**:107–113.

15. Kurniawan A, Sisnanda VOA, Trilestari K, Sunarsb J, Indraswata N, Ismadji S: **Performance of durian shell waste as high capacity biosorbent for Cr(VI) removal from synthetic wastewater.** *Ecol Eng* 2011, **37**:940–947.
16. Ho YS, Chiu WT, Wang CC: **Regression analysis for the sorption isotherms of basic dyes on sugarcane dust.** *Bioresour Technol* 2005, **96**:1285–1291.
17. Brahimi R, Bessekhoud Y, Nasrallah N, Trari M: **Visible light CrO_4^{2-} reduction using the new $\text{CuAlO}_2/\text{CdS}$ hetero-system.** *J Hazard Mater* 2012, **219–220**:19–25.

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