Full Length Research Paper

Biosorption of nickel (II) ions from aqueous solutions by tapioca peel

Panumas Promthet* and Pinthita Mungkarndee

Department of Environmental Engineering, Khon Kaen University, Khon Kaen, Thailand.

Tapioca peel, waste from native tapioca starch industry in Thailand, was used for the biosorption of nickel from aqueous solution. The experimental parameter focuses on the influence of contact time, solution pH, initial concentration and temperature using batch experiments. The results indicated that the biosorption process was relatively fast, and equilibrium was reached after about 30 min of contact. At pH 5, the nickel removal reached a maximum value. The kinetics and equilibrium data was best-fitted pseudo second-order and Langmuir isotherm indication monolayer chemisorption with maximum capacity 20.37 mg/g. The biosorption process was endothermic and spontaneous in nature. Fourier transform infrared spectroscopy (FTIR) analysis revealed that hydroxyl and carboxyl groups of tapioca peel were mainly responsible for the biosorption of nickel. The regeneration experiments showed that the biosorption capacity of tapioca peel was a total slight decreased 8.8% for five cycles. Tapioca peel in this work has high biosorption capacity that can be used as alternative biosorbent for treatment to remove nickel from wastewater in an efficient and economical way.

Key words: Biosorption, desorption, tapioca peel, regeneration, nickel removal.

INTRODUCTION

Water pollution by heavy metals is an important ecological and environmental issue in Thailand over the last two decades. Nickel is one of the toxic pollutants and it can cause liver and kidney diseases, pulmonary fibrosis, skin dermatitis and chronic headaches. Industrial effluents from nickel electroplating, battery, mining and metallurgy of nickel, aircraft industries, pigments, and ceramic industries are the major sources of nickel contaminants in water resources (Reddy et al., 2011). The best available technologies for the removal of nickel

from wastewater are ion exchange, chemical precipitation, reverse osmosis, and evaporation. However, all these methods have disadvantages like high capital and operation cost or not suitable for small-scale industries.

Biosorption is one alternative that should be of concern to existing method, the advantages of this method over conventional treatment include high efficiency in metal removal from solutions, short operation time, possibility of metal recovery and low cost or free of biosorbent (Alluri

*Corresponding author. E-mail: panumaspt@gmail.com. Tel: +66042835232.

et al., 2007). There are many researchers who used agricultural wastes as biosorbent such as black carrot residues (Guzel et al., 2008), coir pith (Ewecharoen et al., 2008), olive pomace (Nuhoglu and Malkoc, 2009), orange peel (Liang et al., 2010), cashew nut shell (Kumar et al., 2011), cocos mucifera (Asiagwu et al., 2013) and papaya seed (Chithra et al., 2014) for removal of nickel.

Tapioca or cassava is an annual tuber crop grown widely in tropical areas. Currently, Thailand is also the world's largest exporter of tapioca products, including starch, pellets, and chips, with an average of 6 to 7 million tons/year. However, tapioca industry is produced in large quantities as wastes and creating environmental problems. Finding the utilization of tapioca peel, which large quantities is one of the challenge tasks.

The aim of this work was to study the effect of parameters as contact time, solution pH, initial concentration, temperature and reuse in several repeated biosorption-desorption cycles. FTIR was used to analyze functional groups before and after biosorption of nickel ions. Adsorption isotherms, kinetics and thermodynamic were investigated, and the various models were used to explain the biosorption mechanism.

MATERIALS AND METHODS

Preparation of the biosorbent

Tapioca peel waste generated in the native tapioca starch production process from the J. Charoen Marketing Co., Ltd., Chiangkan District, Loei Province, Thailand, were washed with distilled water and dried in an oven at 80°C for 48 h. Tapioca peel were then crushed and sieved to obtain regular size (between 0.425-2.36 mm) and stored in a desiccator for further experiments.

Instrumentation and metal solutions

The functional groups of tapioca peel before and after adsorption were analyzed by FTIR spectroscopy (Bruker, Tensor 27), the analysis were carried out using KBr disc method and the spectra wavenumber varying from 400 to 4000 cm^{-1}. The concentrations of nickel in the solutions were analyzed by AAS (Shimadzu, AA-6200). All chemicals used in this work were analytical grade purchased from Loba Chemie (Mumbai, India). The stock solution was prepared by dissolving required amount of $Ni(NO_3)_2 \cdot 6H_2O$ in distilled water. The pH of solutions was adjusted by pH meter (Mettler-Toledo, S20) using 0.1 M HNO_3 and 0.1 M NaOH.

Biosorption experiments

The biosorption features of tapioca peel were performed as a function of contact time, solution pH, metal concentrations and temperatures. The biosorption studies of nickel measurements were carried out using batch experiments, 1.0 g of tapioca peel and 100 ml metal solutions in Erlenmeyer flasks was agitated at 200 rpm in orbital shaker (Forma Scientific, model 420) at temperature 35°C and particular for a given time. The solution was separated by filtering through a fiberglass filter and analyzed using AAS. The experiments were carried out by varying the contact time (5 to 120 min), initial pH (2 to 6), initial metal concentration (25 to 500 mg/l)

and the temperature (5 to 55°C). The biosorption percentage and capacity of nickel from solution were calculated as follows:

Biosorption capacity $\quad q_e = \frac{(C_0 - C_e)V}{m}$

(1)

Biosorption percentage % $= \frac{(C_0 - C_e) \times 100}{C_0}$

(2)

Where, qe is equilibrium concentration in solid phase (mg/g), Ce is equilibrium concentration in liquid phase (mg/l), C_0 is initial concentration (mg/l), V is volume of solution (l), and m is biosorbent weight (g).

Desorption experiments

Desorption studies were carried out using batch experiment. 1 g of tapioca peel with 100 ml of nickel (50 mg/l) in Erlenmeyer flasks at solution pH 5 was agitated at 200 rpm on the orbital shaker at temperature 35°C. The solution was filtered after 60 min, and the filtrate was analyzed for the nickel. The nickel-loaded tapioca peel was then washed with distilled water and desorbed with 100 ml of 0.1 M HCl solution and then filtered after 60 min. The filtrate was analyzed by AAS. The same procedure was repeated by five consecutive biosorption-desorption cycles.

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on the biosorption of nickel onto tapioca peel was studied at contact time 5-120 min. The results show (Figure 1) two phases of biosorption. At first, the rapid phase, the biosorption increased rapidly during the first 5 min. After that, the percentage removal increased slowly until the biosorption equilibrium was established at 30 min when the removal was 68.37%. The initial rapid phase is attributed to the abundant availability of surface active sites on tapioca peel, and with the gradual occupancy of these sites by nickel ions and the biosorption process becomes less efficient in the second slower phase (Saeed et al., 2005).

Effect of solution pH

The effect of solution pH on the biosorption of nickel onto tapioca peel was studied at pH 2.0-6.0. The results indicate that (Figure 2) the biosorption percentage was increased with increasing pH from 2.0 to 6.0. The maximum removal of nickel occurred at pH 5.0 which the removal of nickel was 71%.

The effect of pH on the biosorption of nickel onto tapioca peel can be ascribed to low pH, and the surface of tapioca peel would also be surrounded by hydrogen ions (Ozsoy and Kumbur, 2006), which decrease the nickel interaction with active sites of tapioca peel by
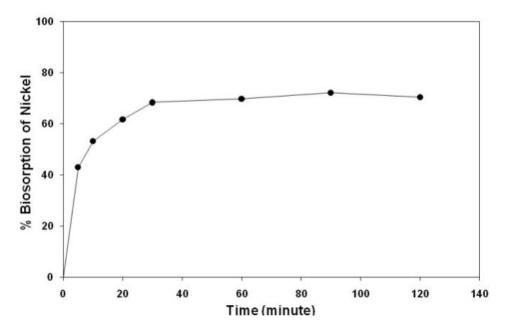
Figure 1. Effect of contact time for biosorption Ni(II) onto tapioca peel.
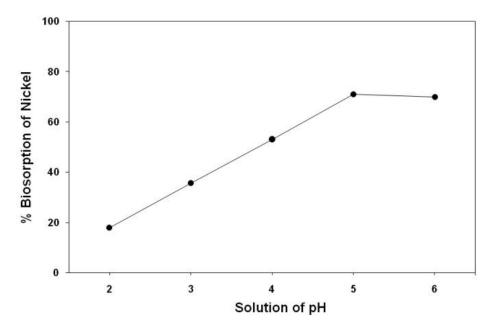

Figure 2. Effect of pH for biosorption of Ni(II) onto tapioca peel.

greater repulsive force, while with an increase in pH, the total surface of tapioca peel became negative and, therefore, biosorption increased.

Biosorption isotherms

The biosorption isotherm of nickel onto tapioca peel was studied concentration ranging between 25-500 mg/l. The results show that the biosorption capacity increased with an increase concentration, when the initial concen-tration increased from 25 to 500 mg/l, the biosorption capacity increased from 2.15 to 17.67 mg/g. This may be attributed to the initial concentration which provides an important driving force to overcome all mass transfer resistance of nickel ions between the aqueous and solid phases, consequently a higher initial concentration of nickel ions may enhance the biosorption capacity. The
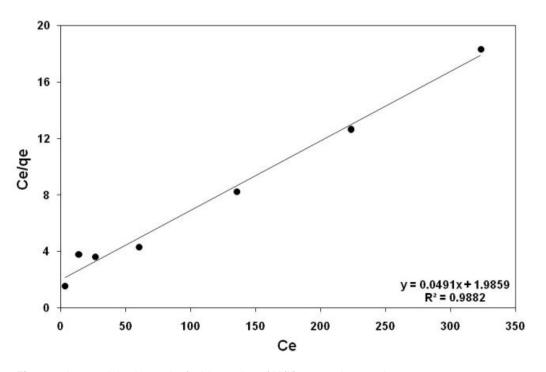
Figure 3. Langmuir isotherm plot for biosorption of Ni(II) onto tapioca peel.

experimental data obtained from studies were tested by using Langmuir and Freundlich isotherm models. The theoretical Langmuir model assumes monolayer coverage of adsorbate over a homogeneous biosorbent surface, each active site interacts with only one adsorbate molecule and the equation is expressed as follows:

$$q_e = \frac{q_{max} \, b C_e}{1 + b C_e}$$

(3)

Where, q_{max} is biosorption capacity (mg/g), and b is the Langmuir constant (l/mg) were obtained from the slope and intercept of plot between C_e/q_e vs. C_e. The theoretical Freundlich model assume based on adsorption on a heterogeneous surface and a multilayer biosorption and the equation is expressed as follows:

$$q_e = K_F C_e^{1/n}$$

(4)

Where, K_F is biosorption capacity and 1/n is biosorption intensity were obtained from the slope and intercept of plot between log qe vs. log Ce.

The results indicate that (Figures 3 and 4) the Langmuir model (R^2 = 0.9882) gave a better fitted experimental data than the Freundlich model (R^2 = 0.9339). The maximum biosorption capacity (q_{max}) and Langmuir constant (b) of tapioca peel obtained in this study were 20.37 mg/g and 0.0247 l/mg. The equilibrium constant (R_L), expressed as in the following equation:

$$R_L = \frac{1}{(1 + b C_0)}$$

(5)

Where, b is Langmuir constant and C_0 is initial concentration. The value of the equilibrium constant (R_L) indicates the biosorption isotherm shape is favorable or not. The value of R_L indicated the type of Langmuir model to be irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) and unfavorable (R_L>1). The R_L was found to be 0.92-0.11 for the concentration of 25-500 mg/l. The values of R_L are all in the range of 0-1 that shows the favorable biosorption of nickel onto tapioca peel.

The comparison of the maximum biosorption capacity of tapioca peel for removal of nickel various biosorbents was presented in Table 1. It shows that the tapioca peel in this work has rather high biosorption capacity. Moreover, it is available in large quantities from tapioca starch industry in Thailand.

Biosorption kinetics

The pseudo first-order and pseudo second-order have been used to explore these biosorption mechanisms. The pseudo first-order, which is also known as of Lagergren and the linear equation, is expressed as follows:
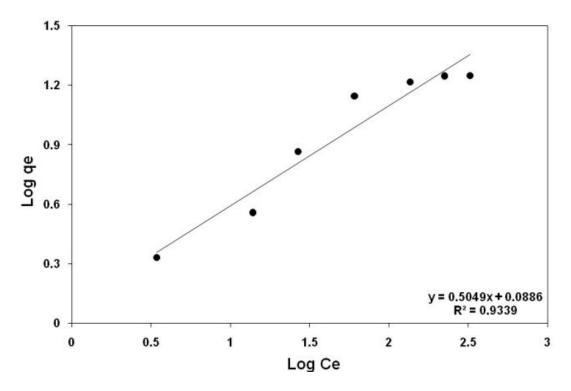
Figure 4. Freundlich isotherm plot for biosorption of Ni(II) onto tapioca peel.

Table 1. Comparison of nickel bisorption capacities (mg/g) of various biosorbent.

Biosorbent	q_{max}	References
Cashew nut shell	18.86	Kumar et al., (2011)
Orange peel	15	Liang et al., (2010)
Olive pomace	14.8	Nuhoglu and Malkoc, (2009)
Coir pith	9.5	Ewecharoen et al., (2008)
Carrot residues	6.51	Guzel et al., (2008)
Papaya seed	5.58	Chithra et al., (2014)
Cocos mucifera	0.09	Asiagwu et al., (2013)
Tapioca peel	20.37	This work

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{6}$$

Where, qe is biosorption capacity of nickel at equilibrium (mg/g); qt is biosorption capacity at time t, and k_1 is the first-order rate constant (min). The values of k_1 and qe were obtained from the slope and intercept of plot between log (qe-qt) vs. t. While, the pseudo second-order, which is known as Ho and McKey model (Ho, 2006), the linear equation is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

Where, k_2 is second-order rate constant (g/mg/min), the values of qe and k_2 were obtained from the slope and intercept of plot between t/qt vs. t.

The values of pseudo first-order and pseudo second-order were listed in Table 2. A comparison of the correlation coefficient (R^2) between the pseudo first-order (<0.9701) and pseudo second-order kinetic (>0.9990); the result show that biosorption of nickel onto tapioca peel followed the pseudo second-order better than the pseudo first-order. Moreover, the values of biosorption capacity (qe) obtained from pseudo second-order was approximate to the experimental value more than the

Table 2. Kinetic parameters of pseudo first-order and pseudo second-order model.

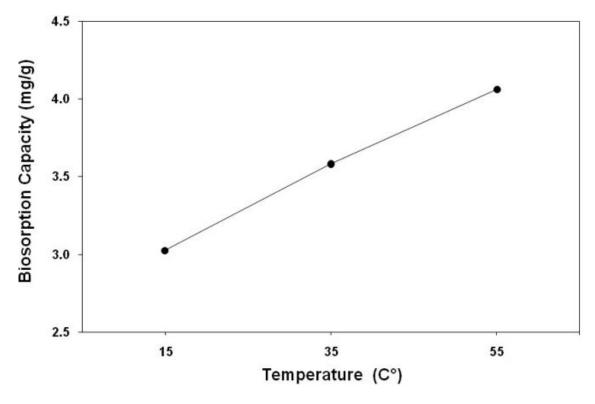|	Pseudo first-order model					Pseudo second-order model			
C_0	$qe_{(exp)}$	k_1	$qe_{(cal)}$	R^2	C_0	$qe_{(exp)}$	k_2	$qe_{(cal)}$	R^2
25	2.01	0.045	0.96	0.9701	25	2.01	0.096	2.10	0.9995
50	3.61	0.045	1.36	0.8741	50	3.61	0.073	3.72	0.9992
100	7.39	0.085	2.93	0.8671	100	7.39	0.041	7.81	0.9990

Figure 5. Effect of temperature for biosorption of Ni(II) onto tapioca peel.

value of pseudo-first order. Therefore, the rate controlling step of nickel biosorption onto tapioca peel might be chemisorption involving valency forces through the sharing or exchange of electrons between the tapioca peel and nickel ions.

Biosorption thermodynamic

To describe thermodynamic behavior for biosorption of nickel onto tapioca peel, temperatures used in this study were 15, 35, and 55°C. The results show that, when the temperature increased from 15 to 55°C, the biosorption capacity of nickel was raised from 3.02 to 4.05 mg/g (Figure 5). The increase in biosorption capacity of tapioca peel at higher temperature may be attributed to the enlargement of pore size or activation of some

components available at the surface of tapioca peel which respond to nickel biosorption. The thermodynamic distribution coefficient (K_D), is expressed in the following equation:

$$K_D = C_A/C_e \qquad (8)$$

Where, C_A is equilibrium metal concentration on the surface biosorbent (mg/l), and Ce is equilibrium metal concentration in the bulk solution (mg/l). The value of free energy change ($\Delta G°$) was calculated from the following equation:

$$\Delta G° = -RT\ln K_D \qquad (9)$$

Where, R is gas constant (8.314 J/mol/K), and T is Temperature (°K). The values of entropy change ($\Delta S°$)
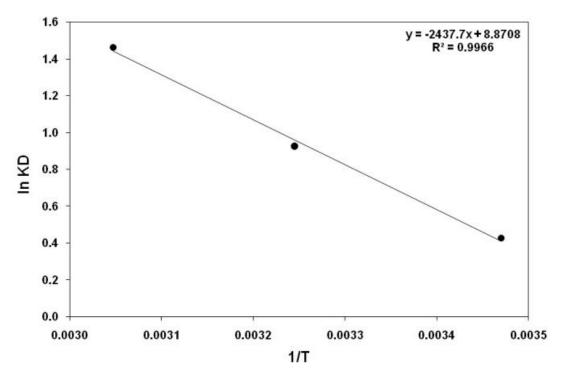
Figure 6. Thermodynamic plot for biosorption of Ni(II) onto tapioca peel.

and enthalpy change (ΔH°) were calculated from the following equation:

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{10}$$

The ΔS° and ΔH°can be obtained from slope and intercept of plot between $\ln K_D$ vs. 1/T (Figure 6). The value of free energy change (ΔG°) was calculated to be −2.98, −5.02, and −7.06 kJ/mol. The ΔS° and ΔH°was found to be 102 J/mol K and 26.41 kJ/mol for the biosorption of nickel at 15, 35, and 55°C. The negative value of ΔG° indicated the spontaneous nature and the positive values of ΔS° show that the freedom of nickel is not too restricted in the tapioca peel. The positive value of ΔH° indicated that the biosorption of nickel onto tapioca peel was the endothermic process.

Organic functional groups analysis of tapioca peel

The FTIR spectra of native tapioca peel (Figure 7a), indicated the presence of several functional groups. The adsorption peaks at 3431 cm^{-1} was due to hydroxyl groups (–OH) and the peaks at 2929 cm^{-1} was likely attributable to the presence of γ(C–H) bonds in carboxyl group (–COOH). The peak observed at 1760 cm^{-1} was the stretching vibration of C=O bond due to non-ionic carboxyl groups (–COOH, –COOCH$_3$), and may be assigned to carboxylic acids or their esters. The peaks at

1652 cm^{-1} indicated C=O stretching in carboxyl groups and the peak observed at 1031 cm^{-1} was assigned to C–O stretching of alcohols and carboxylic acids. The FTIR spectrum of nickel-loaded tapioca peel (Figure 7b), showed that the stretching vibration at 3431 cm^{-1} was shifted to 3426 cm^{-1}. The peak of carboxyl was shifted from 2929 to 2922 cm^{-1} and the stretching vibration at 1760 cm^{-1} was shifted to 1748 cm^{-1}. The stretching vibration at 1652 cm^{-1} was shifted to 1637 cm^{-1} and the peak of C–O group was shifted from 1031 to 1034 cm^{-1}, respectively. These shifts of FTIR spectrum of tapioca peel after the biosorption of nickel may be attributed to the chemical interactions as ion exchange between hydrogen atoms of hydroxyl and carboxyl groups on the surface of tapioca peel and nickel ions were mainly involved in the biosorption process.

Regeneration and reuse of tapioca peel

The regeneration of tapioca peel was repeated for up to five biosorption-desorption cycles using 0.1 M HCl. The results showed that the biosorption capacity of tapioca peel decreased with an increasing number of cycles (Figure 8). After a sequence of five cycles, the biosorption capacity of tapioca peel was totally reduced by 8.8% which may be due to the loss of tapioca peel weight during repeated biosorption-desorption cycles. These results show promising regeneration potential of
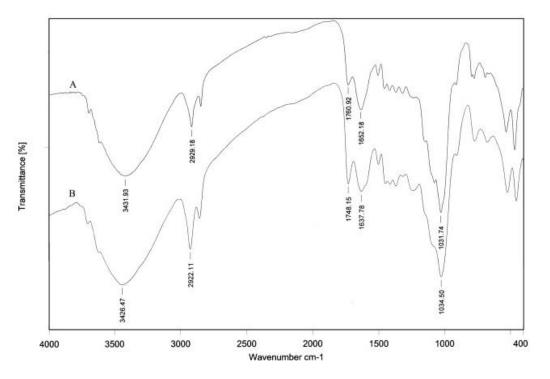
Figure 7. FT-IR spectra of native tapioca peel (A) and Ni(II) loaded tapioca peel (B).
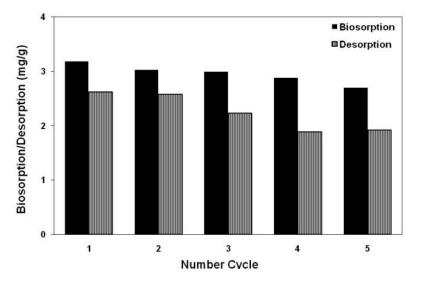

Figure 8. Biosorption-desorption of Ni(II) onto tapioca peel in five repeated biosorption-desorption cycles.

the tapioca peel. This property of tapioca peel may be utilized by small-scale treatment to remove nickel ions from wastewater in an efficient and economical way.

Conclusions

The biosorption of nickel onto tapioca peel was found to be dependent on operating variables such as contact time, solution pH, metal concentration, and temperature. The kinetic studies revealed that the biosorption process followed the pseudo second-order, and Langmuir isotherm model was fitted well with the experimental data. The thermodynamic parameters showed the biosorption process which was endothermic and spontaneous in nature. FTIR analysis revealed that the main functional

groups involved in the biosorption of nickel onto tapioca peel were hydroxyl and carboxyl groups. The regeneration experiments showed that the biosorption capacity of tapioca peel was a total slight decrease by 8.8% for five cycles.

Tapioca peel in this work has high biosorption capacity that can be used as alternative biosorbent for treatment to remove nickel ions from wastewater. Moreover, it is available in large quantities from tapioca starch industry in Thailand. The optimum conditions recorded in this study can be further applied to design in industrial scale for the economical treatment of industrial wastewater.

Conflict of interests

The authors did not declare any conflict of interest.

REFERENCES

Alluri HK, Ronda SR, Settalluri VS, Bondili JS, Suryanarayana V, Venkateshwar P (2007). Biosorption: An eco-friendly alternative for heavy metal removal. Afr. J. Biotechnol. 6(25):2924-2931.

Asiagwu AK, Owamah HI, Christopher IO (2013). Kinetic Model for the Sorption of i(II), Cu(II) and Zn(II) onto *Cocos Mucifera* fibre waste biomass from aqueous solution. J. Chem. Eng. Process. Technol. 4(2):1-7.

Chithra K, Lakshmi S, Jain A (2014). *Carica* papaya seed as a biosorbent for removal of Cr(VI) and Ni(II) ions from aqueous solution: thermodynamics and kinetic analysis of experimental data. Int. J. Chem. React. Eng. 12(1): 91-102.

Ewecharoen A, Thiravetyan P, Nakbanpote W (2008). Comparison of nickel adsorption from electroplating rinse water by coir pith and modified coir pith. Chem. Eng. J. 137(2):181-188.

Guzel F, Yakut H, Topal G (2008). Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II), and Cu(II) from aqueous solution by black carrot residues. J. Hazard. Mater. 153(3): 1275-1287.

Ho YS (2006). Review of second-order models for adsorption systems. J. Hazard. Mater. 136(3):681-689.

Kumar PS, Ramalingam S, Kirupha SD, Murugesan A, Vidhyadevi T, Sivanesan S (2011). Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design. Chem. Eng. J. 167(1): 122-131.

Liang S, Guo X, Feng N, Tian Q (2010). Effective removal of heavy metals from aqueous solutions by orange peel xanthate.   Trans. Nonferrous Met. Soc. China. 20(1):187-191.

Nuhoglu Y, Malkoc E (2009). Thermodynamic and kinetic studies for environmentally friendly Ni(II) biosorption using waste pomace of olive oil factory. Bioresource Technol. 100(8): 2375-2380.

Ozsoy HD, Kumbur H (2006). Adosrption of Cu(II) ions on cotton ball. J. Hazard. Mater. 136(3):911-916.

Reddy DHK, Ramana DKV, Seshaiah K, Reddy AVR (2011). Biosorption of Ni(II) from aqueous phase by *Moringa Oleifera* bark, a low-cost biosorbent. Desalination 268(1-3): 150-157.

Saeed A, Iqbal M, Akhtar W (2005). Removal and recovery of lead(II) from single and multi metal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). J. Hazard. Mater. 117(1):65-73.