

Imprinted Nickel-Cobalt Chitosan As A Specific Adsorbent Of Nickel (Ni^{2+}) And Cobalt (Co^{2+})

Muhammad Qaddafi, Wahid Wahab, Nursiah La Nafie, Paulina Taba

Abstract: The The research for alternative and innovative treatment techniques has focused attention on the use of double imprinted Nickel Cobalt as adsorbent of nickel (Ni^{2+}) and Cobalt (Co^{2+}). The experiments were done as batch processes. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, pH, Ni(II) and Co(II) ion concentration, and IR spectrum. Kinetic experiments revealed that adsorption was rapid and equilibrium was achieved in 180 min with pseudo second order models. The adsorption data fit well with the Langmuir isotherm models. The adsorption capacity calculated from the Langmuir isotherm was 76.92 mg/g at pH 5 for Ni(II) and 29.41 mg/g at pH 5 for Co(II). The adsorption of Ni(II) and Co(II) was studied by FTIR spectrophotometry, which suggested that the presence of Ni(II) and Co(II) ions in the double imprinted adsorbent affected the bands corresponding to amine and hydroxyl.

Keywords: imprinted, adsorption; Ni(II) and Co(II); Sorption isotherm.

1 INTRODUCTION

Many metal ions are essential as trace elements but at higher concentrations they become toxic, including nickel and cobalt. Exposure to nickel and cobalt can produce anemia, disease of the liver and kidneys, brain damage and ultimately death (Jain et al., 1989) Nickel and cobalt contamination released into the environmental as a result of different activities such as metal production, plating facilities, mining activities, etc. While the removal of toxic metals from industries wastewaters has been practiced for several decades, the effectiveness, and particularly the cost effectiveness, of the most common physical-chemical processes is limited (Figuera, et al., 2000). Because expensive consideration, hence the developed some innovative methods such as ultra filtration with polymer (Guibal, 2004) sorption onto purified biopolymers (Jang et al., 1995; Bailey et al., 1999; Babylon and Tonni, 2003), adsorptive using coated sands (Benjamin et al., 1996; Bailey et al., 1999), adsorption on magnetic iron oxides adsorption (Chen et al, 1991), and adsorption (Volesky, 1990). The process of heavy metal removal with the use of biological materials is called bio-adsorption. The potential of biological materials has been investigated as an alternative to treat low metal-bearing wastewaters. One of bio-sorbents that is widely investigated as heavy metal adsorbent is chitosan (Herwanto and Santoso, 2006). Chitosan has active groups such as -OH and -NH₂ so it is possible to use as an adsorbent. Disadvantages of chitosan that is not able to cope with metals at low pH, also its ability to be easily influenced by the anions in waters. To overcome these shortcomings, modification by means of cross-linking of the polymer chains is recommended in order to form a cross-linked chitosan (Cao et al., 2001). The Effective use of adsorbents to attract the target of metal ions in polluted waters sometimes decreases. This is mainly due to the presence of other metal ions have a greater affinity to the adsorbent. So that,

it is necessary for the modification of the adsorbent through certain techniques so that the adsorbent can bind metal ions selectively. To maintain and improve the selectivity of the adsorption capacity of chitosan cross-linked to certain heavy metals then performed a printing technique of metal ions on chitosan amino group first, then cross-linked with a cross-linking agent, and subsequently issued with a metal ion chelating (Varma et al., 2004; Chen et al., 2008). This method of printing on a metal ion adsorbent subsequent desorption with the metal ion chelating chemical compounds known as imprinting method. In a periodic system, nickel and cobalt contained an element of transition group VIII B at 4th period. Nickel with atomic number 28 and cobalt 27, practically Showed similar electron configurations. In nature, the existence of these two metals are always found together. In the production of nickel ore involve, always the presence of a mixture of cobalt metal alloys. Thus, these two metals are found together in polluted waters. With the atomic radius of almost the same, then the nickel and cobalt can compete in the adsorption process by the adsorbent. Nickel ion imprinted chitosan may be able to adsorb the cobalt ions, and vice versa cobalt ion imprinted chitosan can adsorb metal ions nickel. In continuing the search for efficient diverse heavy metal adsorbers, imprinted-nickel-cobalt at chitosan will investigated. The aim of this study was to explore the possibility using imprinted nickel-cobalt for removing Ni(II) and Co(II) ions from aqueous solution. The influence of various factors, such as, contact time, initial pH and initial metal ion concentration on the sorption capacity were studied. The pseudo first-order and pseudo second order were used to analyze kinetic models for Ni(II) and Co(II) adsorption. The Langmuir and Freundlich models were used to analyze the adsorption too equilibration. The functional groups play a role with Ni(II) and Co(II) sorption were analyze with FTIR spectra.

2 METHOD

2.1 Preparation Material

A total of 1 gram of chitosan dissolved in 50 ml of a mixture of ions Ni(II) and ions Co(II) 3000 mg.l⁻¹, then stirred until a homogeneous gel is formed and allowed to stand for 24 hours. Syringe gel dripped through a syringe into 50 ml of 0.2M NaOH solution were added 1 ml of ethanol, then stirred for 1 hour to form granules (beads). Filtered and the filtrate beads collected for metal analysis by AAS. Beads put in 50 ml of 5% epichlorohydrin, then stirred for 6 hours, the solution was

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filtered with a filter paper and washed with distilled water until neutral. Nickel and cobalt contained in the residue in 50 ml of desorption with 0.05M EDTA acid solution, by stirring for 3 hours. The mixture was filtered with whatman filter paper 42. Filtrate collected for metal analysis by AAS. Residues resulting in activation with 50 ml of 0.1M sodium hydroxide solution, stirred for 1 hour, filtered, and the residue was washed with distilled water until neutral. Results washing dried in an oven at a temperature of 60 °C until a constant mass is then crushed and sieved to 80 mesh size. The adsorbent result is called the Imprinted Nickel-Cobalt Chitosan. The dried adsorbent was ground and sieved to Obtain uniform material and it was then stored in a desiccator for use.

2.2 Solutions

The stock solutions of Ni(II) and Co(II) were prepared in de-ionized water using Ni(NO₃)₂ and Co(NO₃)₂ (analytical reagent grade). All working solutions were prepared by diluting the stock solution with de-ionized water.

2.3 Experiment

Batch experiments of adsorption at constant temperature (27 °C) in erlenmeyer flasks, stirred in a reciprocal shaker (150 rpm) for 180 min. In all sets of experiments 0.2 g of powder of adsorbent was thoroughly mixed into 50 ml solution of Ni(II) and Co(II). After shaking the flasks, the reaction mixtures were filtered to remove particulates and the filtrate were analyzed by atomic absorption spectrophotometer for the concentration of Ni(II) and Co(II) measurement. The sorption capacity of metal ions is the concentration of metal ions on the adsorbent and can be calculated based on the mass balance principle where

$$q = \frac{V(C_i - C_f)}{m}$$

Several sets of experiments were conducted to determine the influence of contact time, effect of pH, and metal concentration. Fresh-dried imprinted nickel-cobalt chitosan adsorbents were tested with Fourier transform infrared spectrometer (FT-IR) (Shimadzu 8400S) to Evaluate the functional groups that might involve in the sorption of nickel and cobalt.

3 RESULTS AND DISCUSSIONS

3.1 Characterization of adsorbents

Functional group of Imprinted Nickel-Cobalt Chitosan was determined using infrared spectroscopy approach. Through the analysis of the FTIR spectra, several functional groups that Affect the binding of metal ions can be determined. Adsorption bands Chitosan Raw materials before modified Compared to the Imprinted Nickel-Cobalt Chitosan can be seen in Fig 1 and the difference can be-identified as shown in Table 1. The difference adsorption bands of chitosan raw materials before and after modification indicates that there is interaction between the functional groups of chitosan with epichlorohydrin and the ionic Ni (II) ions and Co (II) ions. This interaction causes a shift of the adsorption band between chitosan raw materials prior to modification after modification. Of all the existing functional groups on chitosan, hydroxyl and amine functional groups are functional groups that play a role in the shift of adsorption bands.

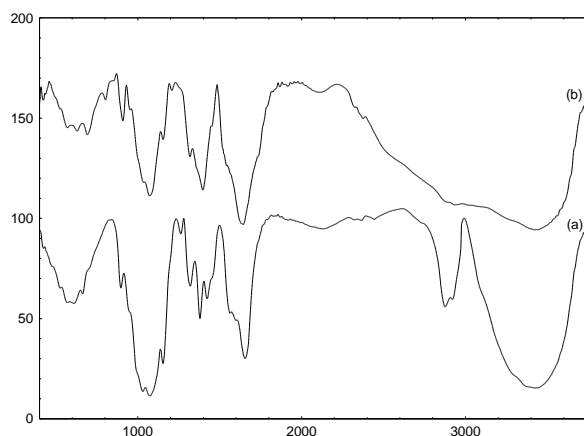


Fig 1. FTIR spectra of chitosan raw material (a) and imprinted nickel-cobalt chitosan (b).

TABLE 1

Comparison of FTIR spectra of chitosan raw materials before modification and after modification

Frequency (cm ⁻¹)		Notes
(a)	(b)	
3421.72	3441.01	-OH stretching N-H
2922.16	3032.10	C-H in -CH ₂
2875.86	2933.73	-CH ₃
1379.10	1396.46	bending vibration of methilen
1423.47	1452.40	Bending vibration of methyl
1654.92	1643.35	Vibration N-H
1562.34	1543.05	Vibration -NH ₃ ⁺
1153.43	1155.36	Vibration asymetry of CO
896.90	908.47	Saccharide structure of chitosan

3.2 Effect of pH

pH is a key parameter, because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Adsorption of Ni(II) and Co(II) by Imprinted Nickel-Cobalt Chitosan was studied at pH values of 3, 4, 5, 6 and 7. The effect of initial pH on adsorption Ni(II) and Co(II) is presented in Fig 2. As shown in Fig 2, the uptake of free ionic Ni(II) and Co(II) depends on pH, where optimal metal sorption occurs at pH 5 and then declining at higher pH. At pH values lower, Ni(II) and Co(II) sorption was inhibited, possibly as a result of the competition between hydrogen and Ni(II) ions or hydrogen and Co(II) on the sorption sites, with an apparent preponderance of hydrogen ions, which restrict the approach of metal as in consequence of the repulsive force. After pH increased, the ligands such as amine groups and hydroxyl, in adsorbent would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing

the adsorption onto the cell surface (Antunes, 2003). The decrease in the adsorption with increase of pH (pH 5) may be due the decrease in electrostatic force of attraction between the sorbent and sorbate ions. Meanwhile the lower sorption at pH 6, and 7 than pH 5 earn by hydrolysis Ni(II) and Co(II) onto the solution.

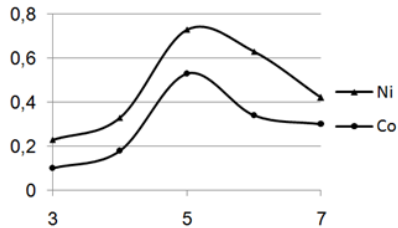


Fig 2. Ni(II) and Co(II) sorption by adsorbent in function of pH. Initial concentration of Ni(II) and Co(II) 5 mg.l⁻¹; adsorbent 0,2g/50 ml; contact time 180 min 150 rpm.

3.3 Effect contact time onto adsorption

The purpose of this experiment was the determination of the contact time required to reach the equilibrium between dissolved and solid-bound sorbat. Equilibrium time is a function of many factors, such as type of biomass (number and kind of adsorption sites), size and form of biomass, physiological state of biomass (active or inactive, free or immobilized).

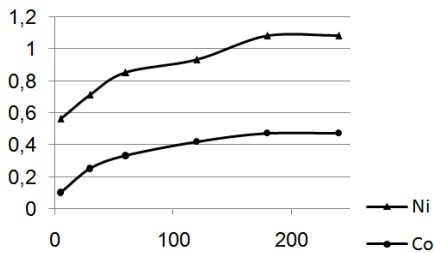
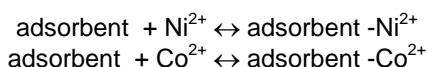


Fig 3. Ni(II) and Co(II) sorption by adsorbent in function of contact time. Initial concentration ions metal: 5 mg.l⁻¹, adsorbent 0,2g/50ml. The kinetic parameters are necessary to determine the best operational conditions in a continue process of ions removal (Pino et al. 2006). The results that were obtained from the contact time study of adsorption is presented in Fig 3. They indicate an extremely rapid kinetic rate sorption in the first min, 0,56 mg.g⁻¹ and 0,1 mg.g⁻¹ for Ni(II) and Co(II) respectively, and an approach to reach equilibrium in about 180 min, 0,93 mg.g⁻¹ and 0,42 mg.g⁻¹ for Ni(II) and Co(II) respectively. The period of 180 min was therefore considered as the optimum time. The reaction involved the adsorption of Ni(II) and Co(II) from the liquid phase to the solid phase and can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below:



In order to analyze the adsorption kinetics of Ni(II) and Co(II), the linearized pseudo first-order (1) and pseudo second-order (2) kinetic models were applied to data.

$$\ln(q_{eq}-q) = \ln q_{eq} - k_{1,ad} t$$

$$\frac{t}{q} = \frac{1}{k_{2,ad} q_{eq}^2} + \frac{1}{q_{eq}} t$$

Fig 4, 5, 6 and 7 shows a plot of linearized form of the pseudo first-order and pseudo second order respectively model at 5 mg.l⁻¹ initial Ni(II) and Co(II) concentration. The first-order rate constant and the second order constant are compared with the correlation coefficient in table 2. The correlation coefficients for the second-order kinetic model obtained was greater than 0,99. The theoretical q_{eq} value is close the experimental q_{eq} values in the case pseudo second-order kinetics. These suggest that the adsorption system is the second-order model, based on the assumption that the rate limiting step may be the adsorption, provides the best correlation of the data.

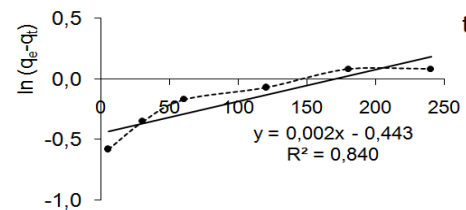


Fig 4. Pseudo first-order sorption kinetics Ni(II) onto adsorbent. Initial concentration of nickel 5 mg.l⁻¹; adsorbent 0,2g/50ml.

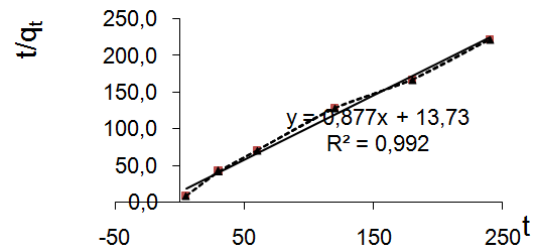


Fig 5. Pseudo second-order sorption kinetics Ni(II) onto adsorbent. Initial concentration of nickel 5 mg.l⁻¹; adsorbent 0,2g/50ml.

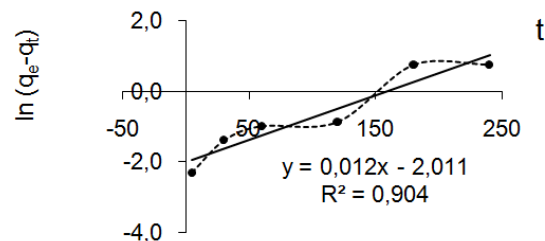


Fig 6. Pseudo first-order sorption kinetics Co(II) onto adsorbent. Initial concentration of cobalt 5 mg.l⁻¹; adsorbent 0,2g/50ml.

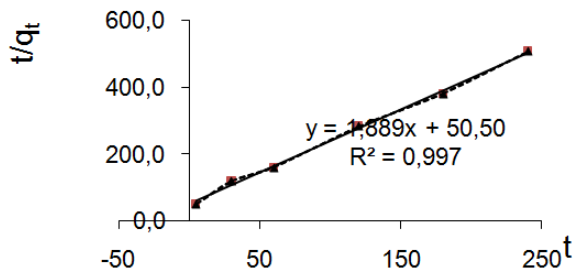


Fig 7. Pseudo second-order sorption kinetics Co(II) onto adsorbent. Initial concentration of cobalt 5 mg.l⁻¹; adsorbent 0,2g/50ml.

TABLE 2

The first-order and the second-order sorption rate constants

Ions metal	First order			Second-order		
	K _{1,ad} (min ⁻¹)	K	R ²	K _{2,ad} (g.mg ⁻¹ min ⁻¹)	K	R ²
Ni(II)	0.002	0.443	0.840	0.877	13.73	0.992
Co(II)	0.012	2.019	0.904	1.889	50.50	0.997

3.4 Sorption Isotherms

The nickel and cobalt sorption capacity by double imprinted Ni(II) Co(II) chitosan adsorbent corresponding to different initial metal concentrations (10, 50, 100, 200, 300 mg.l⁻¹) are shown in Fig 7. The nickel and cobalt sorption is 1,84 mg.g⁻¹ and 1,03 mg.g⁻¹ at 10 mg.l⁻¹ concentration of Ni(II) and Co(II) ions in a aqueous solution. The binding sites are limited keeping biomass loading as constant. With increasing metal concentration, the sorption capacity increased and then stabilized with further increment in the metal concentration up to 200 mg.l⁻¹ with the sorption capacity of nickel and cobalt is 27,39 mg.g⁻¹ 17,71 mg.g⁻¹ respectively. This could be because at higher concentrations, as more ions are competing for the available binding sites, the rate of adsorption decreased, resulting in lower adsorption percentage (Pandey et al., 2007). Ni(II) and Co(II) uptake of the double imprinted Ni(II) Co(II) chitosan adsorbent was evaluated using Langmuir isotherms. The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. The following equation can be used to model the adsorption isotherm:

$$q = \frac{q_{\max} b C_{\text{eq}}}{1 + b C_{\text{eq}}}$$

where q is milligrams of metal accumulated each gram of the adsorbent material; C_{eq} is the metal residual concentration in solution; q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates. The Langmuir isotherm is based on these assumptions (Langmuir, 1918):

- metal ions are chemically adsorbed at a fixed number of well defined sites;
- each site can hold only one ion;
- all sites are energetically equivalent and;
- there is no interaction between the ions;

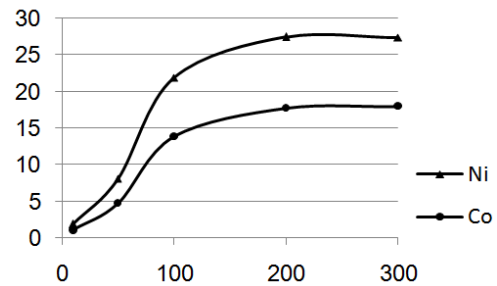


Fig 8. Effect of initial concentration on adsorption of Ni(II) and Co(II) by adsorbent. Contact time 180 min 150 rpm, adsorbent 0,2g/50 ml, pH 5.

When the initial metal concentration rises, adsorption increases while the binding sites are not saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$\frac{C_{\text{eq}}}{q} = \frac{1}{q_{\max} b} + \frac{C_{\text{eq}}}{q_{\max}}$$

The linear plots of C_{eq}/q vs C_{eq} show that adsorption follows the Langmuir adsorption model Fig 8 and 9 for Ni(II) and Co(II) respectively. The correlation coefficient is 0,883 for Ni(II) and 0,860 for Co(II). q_{max} and K_L were determined from the slope and intercept of the plot and were found to be 76,92 mg.g⁻¹ and 0.0016 l.mg⁻¹ respectively for Ni(II) and 29,41 mg.g⁻¹ and 0.0019 l.mg⁻¹ respectively for Co(II) .

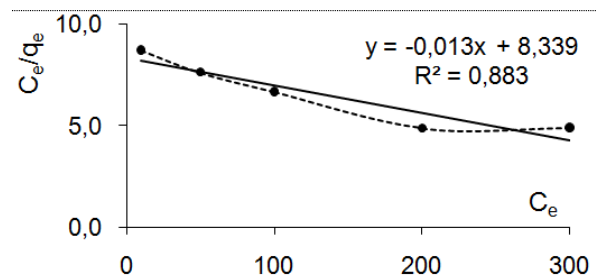


Fig 9. The linearized Langmuir adsorption isotherm of Ni(II) by adsorbent at 27 °C and pH 5

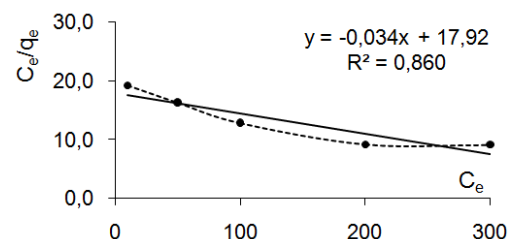


Fig 10. The linearized Langmuir adsorption isotherm of Co(II) by adsorbent at 27 °C and pH 5

TABLE 3

Langmuir and Freundlich isothermal adsorption of Ni(II) and Co by adsorbent at 27 °C and pH 5

Ions metal	First order			Second-order		
	q_{\max} (mg/g)	K_L	R^2	K_f	n	R^2
Ni(II)	76.92	0.0016	0.883	3.3502	1.18	0.950
Co(II)	29.41	0.0019	0.860	6.747	1.118	0.953

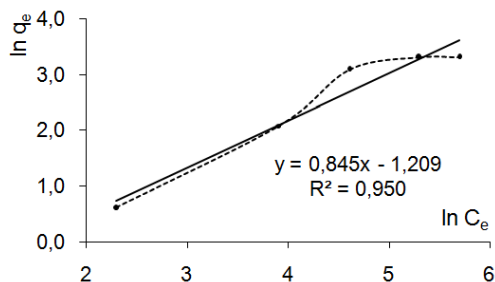
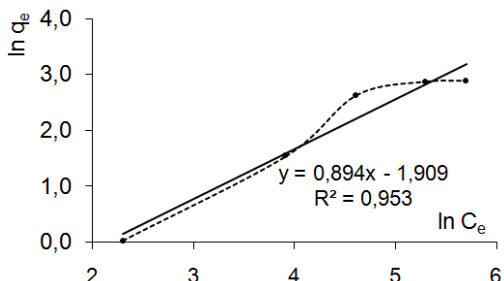
The other isotherm to evaluated Ni(II) and Co(II) uptake onto double imprinted Ni(II) Co(II) chitosan adsorbent are Freundlich isotherm with the equation is given by:

$$q = K_f C_{eq}^{1/n}$$

where C_{eq} is the equilibrium concentration ($mg.l^{-1}$), q is the amount adsorbed ($mg.g^{-1}$) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively. The linearized forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_f + \frac{1}{n} \ln C_{eq}$$

K_f and n were calculated from the slopes of the Freundlich plots Fig 10 and 11. The constants were found to be $K_f = 3,3502$ and $n=1,18$ for Ni(II) and be $K_f = 6,747$ and $n=1,118$ for Co(II). It can be observed from Fig. 8 to 11 that both Freundlich and Langmuir isotherms model exhibited good fit to the sorption data of Ni(II) and Co(II). From Table 3, it is concluded that the Freundlich isotherm model is slight better than Langmuir isotherm model to fit Ni(II) and Co(II) sorption data well cover a concentration range $10 mg.l^{-1}$ to $300 mg.l^{-1}$.

**Fig 11.** The linearized Freundlich adsorption isotherm of Ni(II) by adsorbent at 27 °C and pH 5**Fig 12.** The linearized Freundlich adsorption isotherm of Co(II) by adsorbent at 27 °C and pH 5

3.5 Selectivity of Adsorbent

Adsorption study in a binary system on the adsorbent conducted simultaneously, so that at the time of the interaction, there will be competition between the metal ions to occupy the active sites on the adsorbent. Selectivity adsorption of adsorbent in the system mixture of Ni (II) and Co (II) indicated by the value of the selectivity coefficient distribution ratio, which is calculated based equation

$$K = C_a/C_{eq}$$

$$\alpha = K_{Ni}/K_{Co}$$

$$\alpha = K_{Co}/K_{Ni}$$

K is the distribution coefficient ($L.g^{-1}$), C_a is the adsorption capacity ($mg.g^{-1}$), C_{eq} is the equilibrium concentration of metal ($mol.l^{-1}$), α is the selectivity coefficient, K_{Ni} is the distribution coefficient of Ni (II), and K_{Co} is distribution coefficient of Co (II). Adsorbent selectivity to the metal ions Ni(II) and Co(II) in a mixture of Ni-Co system, as presented in Table 4.

TABLE 4

Distribution coefficient of of KTI-Ni-Co to the metal ions Ni (II) and Co (II) in a mixture of Ni-Co system.

Adsorbent	$K_{Ni}=q/C_{eq}$	$K_{Co}=q/C_{eq}$	$\alpha=K_{Ni}/K_{Co}$	$\alpha=K_{Co}/K_{Ni}$
KTI-Ni-Co	1.21	1.14	1.07	0.94

According to the Table 4, selectivity coefficient ions Ni(II) is higher than Co(II). However, these values did not show significant differences. This is presumably due to differences in particle size of the metal ions Ni(II) is not too much when compared to the particle size of the metal ions Co(II). Moreover, in each adsorbent provided specific cavity of each metal ion with the same comparison, both Ni(II) and Co(II) may adsorbed specific on adsorbent.

3.6 Stability of Adsorbent

Chemical stability test is intended to confirm the alleged success of the synthesis of the adsorbent by dissolving into HNO_3 solution with a pH variation of 1, 2 and 3. Adsorbent synthesized chemically is stable when the weight percentage of acid-soluble material is very small, as presented in Table 5.

TABLE 5

The percentage of insoluble material in the adsorbent

Insoluble Materials Adsorbent		
pH 1	pH 2	pH 3
91	93	96

4 CONCLUSIONS

Imprinted Ni(II) Co(II) Chitosan with epichlorohydrin as a cross-linking agent can be made via the method of imprinting. Adsorbent is able to adsorb metal ions Ni(II) specifically at medium concentrations ($10-200 mg.l^{-1}$) with the adsorption capacity of $27.39 mg.g^{-1}$. Adsorbent is able to adsorb metal ions Co(II) specifically at medium concentrations ($10-200 mg.l^{-1}$) with the adsorption capacity of $17.93 mg.g^{-1}$. The optimum condition takes place at pH 5 with a contact time of 240 minutes and follow order 2 reaction rate equation. Adsorbent selectively adsorb metal ions Ni(II) and Co(II) in binary systems Ni(II) and Co(II) with selective coefficient against

metal ions Ni(II) of 1.07 and the selective coefficient of metal ions Co(II) of 0.94. The use of epichlorohydrin as a cross-linking agent improve the stability of the adsorbent in acid medium.

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