STUDY ADSORPTION: IMMOBILIZED DITHIZONE ON NICKEL SLAG FOR ADSORPTION Cd(II) ION FROM AQUEOUS SOLUTION

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Abstract - This study focuses on the utilization of nickel processing solid wastes called nickel slags as adsorbents for heavy metal adsorption in waters. The nickel slag has been successful modified by activation with HCl (AS) and immobilized with dithizone in an organic solvent (DIS). Study of adsorption of Cadmium was tested with several variables. The results showed that maximum adsorption of cadmium ion at pH 7, optimum mass of AS for cadmium adsorption was 0.2 g and DIS was 0.25 g. Kinetics adsorption for cadmium ions follows a pseudo second order kinetics with optimum adsorption contact time respectively 30 min and 60 min for AS and DIS. Isotherms adsorption for Cd ion follow the Langmuir isotherms with chemisorption process and optimum concentration of Cd ion adsorption of 20 mg L^{-1} and 30 mg L^{-1} for AS and DIS respectively.

Keywords - Nickel Slag, Adsorption, Dithizone

I. INTRODUCTION

The industrial revolution had a negative impact because it caused the production of waste to increase. One of the industrial waste is heavy metals in the waters. Heavy metals waste can be Pb (lead), Cr (chromium), Hg (mercury), Cd (cadmium), Ni (nickel), Cu (copper) and Zn (zinc). The waste especially in waters if not handled properly will cause serious health and environmental problems. To overcome this heavy metals, waste several methods have been applied e.g. ultra-filtration, reverse osmosis, precipitation and adsorption. Hsu et al., (2008) revealed that adsorption has several advantages because it is considered more effective relatively, easier and cheaper to overcome the problem of excess metal concentration in the water[1]. Several studies have been conducted and reported on the adsorption capacity of various types of adsorbents such as kaolin [2], siderite[3], bentonite [4], lignin [5], clay[6], zeolites [7], fly ash [8], bottom ash [9] [10], silica gel [11] [12] and others.

Slag is one of the industrial solid wastes found in metal smelting or mining processes, can be considered as cheap, efficient and selective adsorbents for research. Indonesia is known as one of the largest nickel mining countries in the world, according to research results Josowidagdo (2003) solid waste processing of nickel (slag) produced approximately 300-400 tons of slag per day per electric furnace [13]. The slag which produced in a large volume will have a bad impact in the future if just ignored, so that handling properly is necessary. One solution to handle this waste is to use it. Slag is reportedly utilized as a refactor and mixture material in the manufacture of concrete. In addition, slag can be utilized as adsorbent, but the study of nickel slag as an adsorbent has not been widely reported, especially in Indonesia.

Nickel slag is derived from nickel-processing waste. Generally, nickel slag containing silica (SiO_2) silica, which means that slag can be categorized as a silica-based material similar to other common silica-based adsorbents such as zeolites, silica gel, as well as coal bottom ash which has been successfully reported as a good adsorbent. Addai (2014) also reports on nickel slag as a heavy metal adsorbent without modification. Adsorbent modification is already very common for example for zeolite, bentonite, clay, silica gel, fly ash because the result can significantly improve adsorption capacity such as having good adsorption capacity and selectivity compared to without modification [14]. Modifications can be done in various ways such as activation with acid or base or immobilize another substance into the adsorbent. Several successful modifications have been reported for example modification of bentonite-alginate [15], modified halogen fly ash [16], Amine modified silica gel [17], modification of zeolite-amine [18], natural zeolite-dithizone[19]

Dithizone (diphenylthiocarbazone) is used as one of the additional modified materials. It is the organic complexing compounds that have more than one donor atoms (S and N atoms) and acknowledged has good sensitivity and selectivity to some metals such as Ag, Hg, Cu [20]; Cd and Cu [21] and Pb[22]. So, this present work aims to modified the slag with dithizone, in hope when the nickel slag is immobilized with dithizone the adsorbent will have a good adsorption and selectivity capacity on heavy metal ions especially Cd.

II. DETAILS EXPERIMENTAL

2.1. Materials and Instrumentation

Cadmium Nitrate ($Cd(NO_3)_2$) and dithizone (1,5-diphenylthiocarbazone) were purchased from Merck, Germany. Nickel Slag was obtained from PT. Antam,

Pomala South East of Sulawesi, Indonesia. Organic solvents: toluene and ethanol were of reagent grade and used as received. For all solutions, double distilled water was used and the buffer solutions were prepared by mixing citric acid ($C_6H_{10}O_7$) and sodium citrate ($C_6H_5Na_3O_7{\bullet}_2H_2O$) for pH 3- 7 and sodium dihydrogen phosphate ($NaH_2PO_4{\bullet}H_2O$) and sodium hydrogen phosphate ($Na_2HPO_4{\bullet}12H_2O$) for pH: 7–9 and the pH-value of the resulting solution was checked by pH-meter. The pH measurements were conducted by a TOA pH meter model HM5B calibrated against three standard buffer solutions of pH 4.01, 7,00 and 9.21. Infrared spectra of nickel slag and dithizone-immobilized nickel slag were measured from KBrpellets by a Shimadzu FT-IR/8201 PC spectrophotometer. Cd(II) determination was performed by a GBC 932 AA atomic absorption spectrophotometer at Laboratory of Analytical Chemistry, Chemistry Department, GadjahMada University, Yogyakarta, Indonesia. X-ray diffraction (XRD) spectra of nickel slag and dithizone-loaded nickel slag were recorded on Phillips model PW 3710 BASED XRD spectrophotometer (Shimadzu 6000X, radiation source: Cu, K-lambda 1.5402 nm).

2.2 Activation of slag nickel (AS)

The nickel slag was powdered and sieved with a 250 mesh sieve to obtain a homogeneous particle size. The activation process was carried out by refluxing 20 g of slag in 120 ml of concentrated hydrochloric acid solution (1:1) for 4 hours. The mixture is then filtered and washed with double distilled water until the filtrate is neutral (pH=7). The obtained solids were dried in an oven at 110°C for 6 hours then characterize with XRF, XRD and FTIR

2.3 Dithizone immobilization on nickel slag (DIS)

Nickel slag (4.0 g) was added to 80 mL toluene and mixed with 1.0311 g dithizone in a 500 mL flask. The mixture was heated and stirred for 4 h and the temperature of the mixture is 55°C. The product was filtered and washed consecutively with toluene, ethanol and double distilled water several times until the filtrate showed no characteristic color of dithizone. The dithizone-immobilized nickel slag (DIS) was then dried in an oven at 50°C for 6 h and filtered through 250-mesh filter. The obtained DIS was then characterized and used for adsorption study.

2.4Adsorption study

2.4.1 Effect of pH on the Cd(II) adsorption

The experiment was done by batch system. The adsorbent (10 mg, 200 mesh) was interacted with 10 mL of Cd(II) ion (10 mg/L) solution and the pH of the solution was varied from 3.0 to 8.0 using buffer solution. The mixture was stirred with spin bar and magnetic stirrer for 90 min. The mixtures were then filtered and the concentration of Cd(II) ion in the filtrate was determined by AAS. For a control solution, the same concentration of Cd(II) solution at corresponding evaluated pH was treated in the similar procedure but without the addition of adsorbent. The amount of metal ion adsorbed, q_e(mg/g), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)\,V}{m}$$

where C_0 is the initial metal ion concentration (mg/L), $C_e$is the equilibrium metal ion concentration (mg/L), V is the volume of solution (L) and m is the mass of the adsorbent (g).

2.4.2 Effect of mass adsorbent on the Cd(II) adsorption

The experiment was done by batch system. A similar procedure to that described in the previous section (effect of pH) was applied but the mass of adsorbent was varied 0.05 g, 0.1 g, 0.2 g, 0.25 g, 0.3 g and 0.4 g. The amount of metal ion adsorbed was calculated with the equation:

$$\%R = \frac{C_0 - C_e}{C_0}\, x100\%$$

where C_e is the amount of adsorbed metal ion and C_o is the initial concentration of metal ion.

2.4.3 Effect of contact time on the Cd(II) adsorption

A similar procedure to that described in the previous section (effect of pH) was applied but the stirring/contact time was varied from 5 to 120 min. This experiment was carried out to evaluate kinetic aspects of Cd(II) ion adsorption on the AS and DIS adsorbent. The obtained data were then evaluated with the equation kinetic.

Tabel.1 Kinetic of equation

Reaction order	Equation
Zero order	$C = C_0 - kt$
Firs order	$\ln C = \ln C_0 - kt$
Second order	$\frac{1}{C} = \frac{1}{C_0}$ kt
Third order	$\frac{1}{C^2} = \frac{1}{{C_0}^2} + kt$
Pseudo first-order	$\ln (q_e - q_t) = \ln(q_e) - k_1 t$
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t$

2.4.4. Effect of initial concentration of metal ions on the adsorption capacity

The effect of initial concentration of Cd(II) ions on the adsorption capacity of AS and DIS adsorbent was examined by conducting adsorption experiment in various concentration of Cd(II) ion. The similar procedure to effect pH study was applied but the concentration of Cd(II) was varied in the range of 0–40 mg/L. The common used isotherm models are the Langmuir and Freundlich isotherms. The Langmuir isotherm is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

where $q_m$is the maximum adsorption capacity (mg/g) and b is the Langmuir constant related to the energy of adsorption (L/mg).

The linear form of Freundlich equation is expressed as:

$$Log\ q_e = Log\ K_F + \frac{1}{n} Log C_e$$

where K_F and n are the Freundlich constant related to adsorption capacity and adsorption intensity, respectively

III. RESULTS AND DISCUSSION

3.1 Chemical composition slag

Nickel slag has been activated by HCl (1:1) to remove impurities like other unneeded metal oxides which can interfere with immobilization and adsorption processes [23], and alter siloxane groups (Si-O-Si) on the surface of the slag into silanol (Si-OH) groups in order to make it more effective for adsorption and can facilitate interaction with dithizone during immobilization. Chemical content of adsorbent is important because it play an important role in the adsorption process.

Table.2 Chemical content slag nickel

Nickel Slag	% Composition				
	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3
Slag	12.8	2.49	46.9	2.29	30.8
AS	9.55	1.88	60.1	1.71	23.2

Table.2 shows before and after activation and the main content of nickel slag is SiO_2 which is increased from 46.9% to 60.1% because the impurities and some other metal oxides have decreased and even disappeared. SiO_2 is theoretically a solid compound which is inert to acid except HF so that in HCl solution, SiO_2 is difficult to dissolve while other metal oxides are highly soluble.

3.2 XRD pattern of AS and DIS

The characterization of XRD is done to identify crystallinity and mineral structure for slag, AS, DIS and dithizone. Based on Fig.1 the angular diffraction ratio of 27.96 (d=3.18Å); 30.95 (d= 2.88Å); and 36.26 (d=2.47Å) corresponds to the diffraction angle 27.21 (d=3.27Å); 30.05 (d= 2.97Å); and 36.68 (d= 2.45Å) which is a mineral clinoenstatie ((Mg, Fe) SiO_4), while for peak 36.26 (d= 2.47Å) and 62.995 (d= 1.47Å) corresponds to a diffraction angle of 35.65 (d= 2.52Å) and 62.57 (d= 1.48Å) characteristic with forsterite minerals ((Mg, Fe) SiO_3).

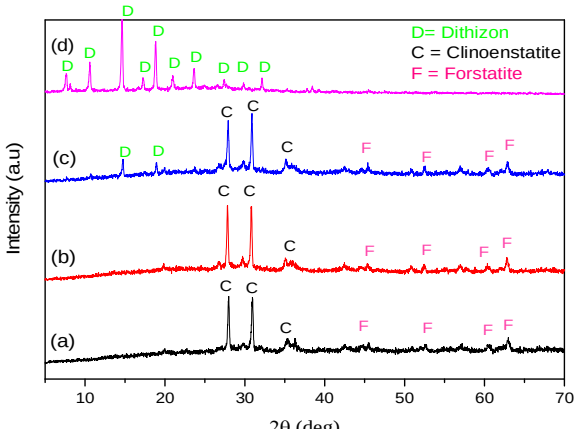

Fig.1 XRD Slag (a), AS (b), DIS (c) dithizone (d)

Thus it can be seen that this nickel slag is composed of most crystalline minerals clinoenstatie and forsterite. The identification of these minerals matches to XRF result in Table.2 that the mostly content of slag are SiO_2, MgO_2 and Fe_2O_3. Furthermore, if we compare the difractogram for the DIS and the standard dithizone, it can be seen that there are 2 highest dithizone peaks in the DIS difractogram at 14.75 (d= 6.002Å) and 18.93 (d= 4.68Å) and several other peaks overlapping with the peak of the nickel slag, the presence of the dithizone peak in the XRD DIS difractogram shows that the dithizone is successfully immobilized in the nickel slag.

3.3 FT-IR analysis for AS and DIS

Characterization with FT-IR aims to look at the functional groups in the adsorbent and to see whether the nickel slag modification with dithizone has been successfully performed. Fig.2(a) shows the nickel slag before activation and immobilization, there is a specific wavenumber to show functional group of nickel slag. Wavenumbers 3425 cm^{-1} and 1627 cm^{-1} show the vibration of -OH group and the bending vibration of H-O-H.

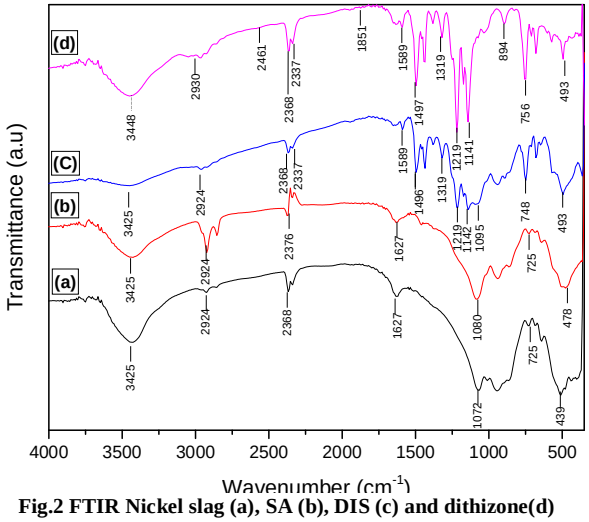

Fig.2 FTIR Nickel slag (a), SA (b), DIS (c) and dithizone(d)

Wavenumbers 1072 cm^{-1} and 439 cm^{-1} show the Si-O vibration of Si-O-Si, Si-O-Al and the Si-O-Si bending vibrations and the wavenumbers 725 cm^{-1} indicating the asymmetrical vibrations of the external linkage. Fig.2(b) shows nickel slag after activation and there is some shift of wavenumber especially in Si-O group. Shift for the Si-O vibration from 1072 cm^{-1} to 1080 cm^{-1} and the Si-O-Si bending vibration from 439 cm^{-1} to 478 cm^{-1}. This is due to the loss of impurities from other metal oxides that covering the slag surfaces so the ratio of SiO_2 composition in the slag increased (according to the XRF analysis data) and the Si-O group interaction becomes stronger. Fig.2(c) shows the nickel slag functional group after immobilization with dithizone and it is seen that the dithizone is successfully immobilized into the activated nickel slag by observing the specific wavenumber dithizone i.e. 1589 cm^{-1}, 1435 cm^{-1}, and 1312 respectively for bending vibrations -NH, N=N bonds and stretching vibrations CN. There are also observed the wavenumbers 2962 cm^{-1}, 1497 cm^{-1}, and 1141 cm^{-1} for the aliphatic C-H vibration, C=C aromatic vibration and group C=S vibration. Another proved that dithizone successfully immobilized with nickel slag there are shift of wavenumbers in SiO_2 group from slag to Si-O vibration from 1080 cm^{-1} to 1095 cm^{-1} and bending vibration Si-O-Si from 478 cm^{-1} to 493 cm^{-1}. This shifted because of the interaction of Si group from nickel slag with the N group from dithizone.

3.2 Study Adsorption

3.2.1 Effect of pH

One of the most important parameters in the process of adsorption of metal ions in an aqueous solution is the pH of the medium [24]. It is observed from Fig.3 that at low pH the amount of adsorbed Cd(II) ion is low, because at lower pH there are more H_3O^+ ions formed so there is competition between Cd(II) ion and H_3O^+ on the adsorbent active site. In addition, at low pH, the surface site of the adsorbent will be protonated and become less advantageous for Cd(II) ion interact with the adsorbent active site due to electrostatic repulsion.

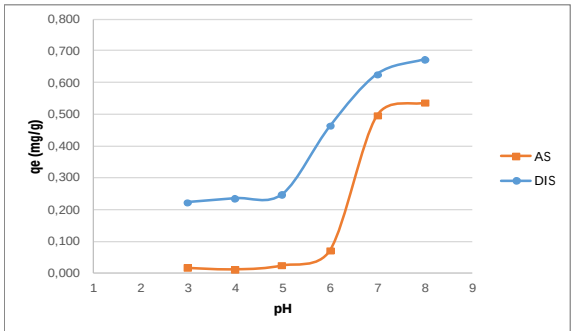

Fig.3 Effect pH of Cd(II) ion adsorption on AS and DIS

The optimum conditions of Cd(II) ion adsorption at pH 7 although at pH 8 the q_e value chart is still increase but the value is not very significant and it is feared that taking the optimum pH at 8 will lead to the precipitation process as it is known that at pH about 8[25]. Cd speciation has already formed as $Cd(OH)_2$ which has a low ksp value in solution so it is possible to precipitate. Several previous studies have been reported analogous with this result, for example Tahervand and Mohsen (2016) reported that Cd(II) ion adsorption was optimum at pH 7[26]. Xue et al., (2009) research for steel slag as adsorbent for Zn and Cd adsorption was optimum at pH 7.1-7.8[27].

3.2.2 Effect of adsorbent mass

Increasing the mass of the adsorbent mass helps provide a large number of active sites that lead to increased adsorption [24]. For understanding the effect of adsorbent mass, there are many factors that can contribute to the effect. The first and most important factor is the adsorption site remains unsaturated during the adsorption reaction. This is due to the fact that the adsorbent mass is increased, there is a less commensurate increase in adsorption resulting from lower adsorptive capacity utilization of the adsorbent. A second cause may be aggregation or agglomeration of sorbent particles at higher adsorbent mass, which will lead to decreased surface area and increase in diffusional path length. The particle interaction at higher adsorbent mass may also lead to the removal of some free metal ions from the sorbent surface [28].

The effect of adsorbent mass on adsorption is shown in Fig.4 where for adsorption Cd(II) ion the optimum mass for AS is 0.2 g and for DIS is 0.25 g. It is seen that the mass variation for AS does not significantly affect compare to DIS which means that the less number of active sites in AS to interact with the metal ions, while for the DIS there is a significant increase which indicating that the more mass of adsorbent the amount of adsorbed substances increases as the number of active sites.

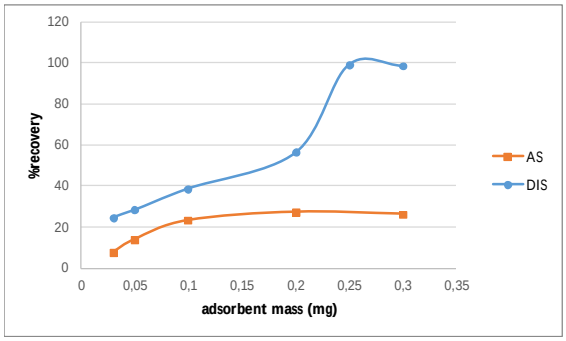

Fig. 4 Graph of Influence mass adsorbent on Cd (II) ion adsorption on AS and DIS

3.2.3 Effect of contact time and kinetic adsorption

The effect of contact time is presented in Fig.5 and for the AS reach optimum at 30 min while the maximum DIS at 60 min. Theoretically, the optimum time shows the equilibrium condition between the adsorbent active site and the metal ion of the

adsorbate in the adsorption process where in equilibrium conditions the amount of metal ions adsorbed is equal to the amount of dissolved metal ions. It was observed that the equilibrium time for DIS was longer than AS, probably due to differences the optimum mass used for adsorption.

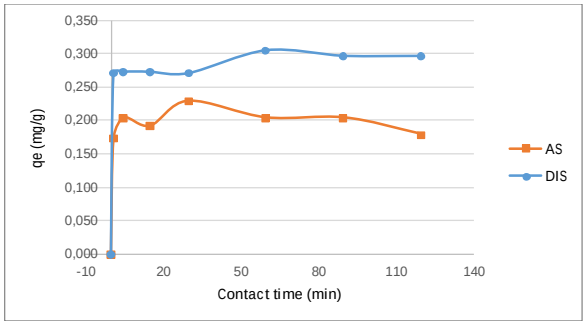

Fig.5 Effect of contact time Cd(II) ion adsorption on AS and DIS

The study of adsorption kinetics is quite important because with this approach it is easy to understand how the dynamics of adsorbate in the adsorption process.Several kinetic approaches have been performed and obtained data as in Table. 3 and Table. 4 Based on the results of the analysis that the adsorption process Cd(II) ion is determined which equations show the most appropriate linear correlation.

Table. 3Various approaches of kinetic equation of Cd(II) ion adsorption on AS and DIS

Reaction order	Equation	R^2	
		Cd(II)	
		AS	DIS
Zero order	$C = C_0 - kt$	0.0081	0.684
Firs order	$\ln C = \ln C_0 - kt$	0.0067	0.6906
Second order	$\frac{1}{C} = \frac{1}{C_0}$ kt	0.0053	0.6968
Third order	$\frac{1}{C^2} = \frac{1}{C_0^2} + kt$	0.0041	0.7027
Pseudo-first-order	$Ln(q_e-q_t)= Ln(q_e)-k_1t$	0.0008	0.9179
Pseudo-Second-order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	0.9911	0.9992

Table. 4 Pseudo-second-order parameter of Cd(II) ion adsorption on AS and DIS

Adsorbent	Pseudo-second-order		
	k ($g.mg^{-1}.min^{-1}$)	q_e ($mg.g^{-1}$)	R^2
AS	2.360	0.186	0.9911
DIS	3.529	0.300	0.9992

From Table.3 the best linear correlation of some kinetic equations shows both AS and DIS follow the pseudo-second-order kinetics. This compatible as adsorption on solid phase adsorption. Previous study also explained that the adsorption of Cu, Cd, Zn and Pb metals followed pseudo-second-order reaction kinetics[27] [9][29][30]. Anari and Alireza, (2015) reported in the study dithizone immobilized of clinoptilolite also followed the pseudo-order kinetics equation [31] [3]. Table.4 shows that DIS rate reaction constants is larger than AS, so the modification with dithizone can increase the reaction rate.

3.2.4 Effect of concentration of Cd(II) ion and isotherm adsorption

The adsorbate concentration in the adsorption study is one of the parameters that is also important. This is because the amount of concentration will affect how much the adsorption interaction with the active site. The greater concentration of adsorbate, will lead to effective interaction, although there is a limit where the active site will be saturated due to limitations of adsorbent capacity. In addition, with this concentration variation we can measure the adsorption pattern associated with the adsorption capacity or we can call the adsorption isotherm. From the observation results shown in Fig.6 the optimum concentration for Cd(II) ion adsorption on AS and DIS respectively at 20 mgL^{-1} and 30 mgL^{-1}. Furthermore, from the figure shown that the q_e value for DIS is greater than AS, which can be interpreted by immobilizing dithizone in slag can increase the adsorption capacity.

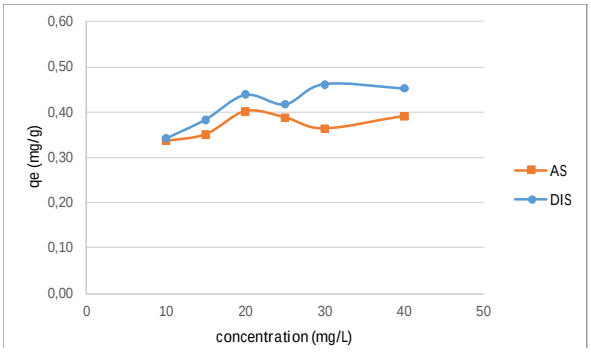

Fig. 6 Effect of concentration Cd(II) ion adsorption on AS and DIS

Table.5 The parameters of Cd(II) ion adsorption isotherm model in AS and DIS

Isotherm		Cd (II)	
		AS	DIS
Langmuir	q_{max} ($mg\ g^{-1}$)	0,391	0,481
	K_L ($L\ mol^{-1}$)	1,871	0,775
	R^2	0,9941	0,9958
	E_{ads} ($KJ\ mol^{-1)}$	-30,3663	-28,181
	R_L	0,013	0,031
Freundlich	K_F ($L\ mol^{-1}$)	0,0708	0,0639
	1/n	0,0626	0,1375
	R^2	0,4046	0,8915

Based on Table.5 shows that the best adsorption correlation values following Langmuir isotherm for both AS and DIS. This means that the adsorbent is homogeneous and when the Cd(II) ion is bonded to

the active site, it will cover the surface forming a monolayer which results in no further adsorption. Table.5 also shows that value of adsorption energy greater than 20 KJ which means that the adsorption occurs as chemical adsorption with negative values indicating the adsorption takes place spontaneously and the RL value is in the range 0 <RL <1 for the adsorption process which indicates Isotherm Langmuir is favored.

CONCLUSIONS

Nickel slag was successfully immobilized with dithizone, as shown in the analysis of XRD and FTIR. Study adsorption shows that the optimum pH of the adsorption Cd(II) ion at 7 for both AS and DIS sample. Mass of adsorbent optimum for AS is 0.2 g and 0.25 g for DIS. The kinetic reaction of this process is following pseudo-second-order kinetic for both sample. Immobilized slag with dithizone can increase rate reaction and increase the capacity of adsorption with the model isotherm followed Langmuir for both AS and DIS.

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