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Intercalated Zn-Cr-[α-$SiW_{12}O_{40}$] as Removal Agents of Cobalt (II) in Watery Phase: Adsorption and Regeneration Study

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ABSTRACT

The Zn-Cr layered double hydroxide was intercalated with polyoxometalate ion $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$ to form Zn-Cr-[α-$SiW_{12}O_{40}$]. Materials were characterized by X-Ray, FTIR, and nitrogen adsorption-desorption and pH pzc analyses. Then materials were applied to remove cobalt(II) from in watery phase. Factors that affecting the adsorption included effect of adsorption time, initial concentration of cobalt(II), and adsorption temperature were systematically examined. The performance of Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] were studied by regeneration process. The results showed that Zn-Cr layered double hydroxide has interlayer galley 7.53 Å. Zn-Cr-[α-$SiW_{12}O_{40}$] layered double hydroxide after intercalation has a unique diffraction peak at 8.62o with an interlayer gallery 10.35 Å; thus interlayer gallery increase 2.82 Å after the intercalation process. The surface area properties were also increased from 31.638 m^2/g to 128 m^2/g after intercalation. The pH pzc of Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] layered double hydroxides were 7.5 and 8, respectively, and adsorption of cobalt(II) was conducted at these pH media. Adsorption of cobalt(II) on both adsorbents follows the pseudo second-order kinetic model and is categorized as physical adsorption in the range of energy 17.628-64.452 kJ/mol. Zn-Cr-[α-$SiW_{12}O_{40}$] follow the Langmuir isotherm model with an adsorption capacity is 45.45 mg/L at 303 K. That capacity is higher than Zn-Cr LDH, which has an adsorption capacity 30.39 mg/L at 303 K. Adsorption of cobalt(II) on layered double hydroxide was sharply decreased after three-time cycles due to sprayed and exfoliated of layered double hydroxide structure.

Keywords: Zn-Cr, layered double hydroxide, intercalated, adsorption, cobalt, polyoxometalate, kinetic, thermodynamic

1. INTRODUCTION

The presence of heavy metal ions in the aquatic environment is toxic not only for marine ecosystem but also human health. Heavy metal ions are produced from electroplating process, mining activities, and also pharmaceutical industry [1]. Heavy metal ions can accumulate

in the environment due to cannot degrade by microorganism and also the toxicity is increased in every step chain food circle thus the erase of heavy metal ions in raw water is become crucial [2]. Numerous treatments have been examined to reduce heavy metals included membrane filtration, ion exchange separation, oxidation, biological treatment, and also adsorption [3]. Among these methods, adsorption is a suitable way to remove heavy metal ions from aqueous solution because simple way, fast process, low cost, and also efficient process with high removal ability [4-5]. The effectivity of adsorption process is depending on ability of adsorbent. Various adsorbents have been used to remove heavy metal ions from aqueous solution such as biomass [5], chitosan [6], algae [7], activated carbon [8], bentonite [9], zeolite [10], and also layered double hydroxide [11]. Heavy metals ion such as cobalt (II) had been widely presents in groundwater and harmful for environment [12]. Thus, the several adsorbents had been conducted to remove cobalt (II) from wastewater. According to Bhatnagar et al., [13] that conducted lemon peel biomass to remove cobalt (II) from wastewater and obtained maximum adsorption capacity 22 mg/g. Musapatika et al., [14] had been reported that pine sawdust was used as adsorbent to remove cobalt (II) and has maximum adsorption capacity 1.11 mg/g. Si/Al zeolite was applied to remove cobalt (II) and obtained maximum adsorption capacity 12.4 mg/g [10]. Coal fly ash had been studied as adsorbent of cobalt (II) in aqueous solution, this treatment obtained adsorption capacity 4.01 mg/g [15]. However, according previous researches did not show the high effectivity of these adsorbent due to their limitation such as small surface area and impurities. Therefore, the researchers had been explored synthesis modified adsorbent such as layered double hydroxide to remove cobalt from wastewater [12-16].

Layered double hydroxide (LDH) is consisting of divalent and trivalent metal ion. Divalent and trivalent ions are commonly from group 2 and group 3 and transition metal ions on periodic elements thus empirical formula of LDH is $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]+xA_x^{-n}mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent ions, A_x^{-n} is anion on interlayer LDH with n valence. Water was found not only on interlayer distance but also as water of crystallization of LDH [17]. The anion on interlayer LDH can be exchanged depending on synthetic conditions and also application of LDH. Anions such as nitrate, sulfate, chloride, and also carbonate were commonly found on LDH and it can be changed with big size anion such as polyoxometalate ion to increased interlayer distance of LDH. Polyoxometalate is inorganic metal-oxygen cluster compounds with addenda and heteroatoms [18]. The general type of polyoxometalate is Keggin type such as $K_3[\alpha\text{-}PW_{12}O_{40}]$ and $K_4[\alpha\text{-}SiW_{12}O_{40}]$. These compounds have been used frequently as intercalant to exchange ion on interlayer LDH. Tarmizi et al., [19] used Keggin ion of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ as intercalant of Ca/Al LDH. Polyoxometalates $[P_2W_{17}]^{10-}$ and $[CoW_{12}]^{5-}$ were used as intercalant of ZnAlFe LDH [20] LDH of NiFe was also intercalated using $[PW_{12}O_{40}]^{3-}$ [21]. All these results showed that unique properties LDH was found after intercalation with polyoxometalate.

In this work, we aimed that Zn-Cr LDH was intercalated with Keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ to form Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDH. Obtained adsorbents were characterized/analyze using XRD, FTIR, and nitrogen adsorption desorption, and pH pzc analyses. Then the materials were used as adsorbent of cobalt(II) from aqueous solution. The biggest source of cobalt(II) is electroplating industrial activity, thus the removal of this ion is vital. Removal metal ions in watery phase was carried out through hat affecting the adsorption included effect of adsorption time, initial concentration of cobalt(II), and adsorption temperature were systematically. The ability of Zn-Cr and intercalated LDH for removal cobalt(II) several times was evaluated by regeneration process.

2. MATERIALS AND METHODS

2.1 Chemicals and Instrumentations

Zinc(II) nitrate, chromium(III) nitrate, sodium carbonate, sodium hydroxide, hydrochloric acid, sodium tungstate, sodium chloride, sodium metasilicate, sodium EDTA, and potassium chloride were obtained from Sigma-Aldrich and Merck. Water was supplied from Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya after several times cycling purification using Purite® ion exchange purification water system. Characterization was conducted using x-Ray Rigaku Miniflex-6000. Sample was scanned at 1°/min at diffraction 5-80°. Infrared spectrum was recorded using FTIR Shimadzu Prestige-21 using KBr method. Analysis of surface area, pore volume, and pore diameter properties were performed using ASAP Micrometric apparatus and sample was vacuum and degassed several time prior analysis. Analysis of cobalt(II) was conducted using UV-Vis spectrophotometer Bio-Base BK UV 1800 PC after complexation of cobalt(II) with 1,10-phenanthroline at wavelength 297.2 nm.

2.2 Preparation of Zn-Cr LDH

Synthesis of Zn-Cr LDH was conducted by coprecipitation method with quite modification according to Oktriyanti et al., [22]. Zinc(II) nitrate (0.1 L, 0.5 M) was mixed with chromium(III) nitrate (0.1 L, 0.1 M). The mixture was constantly stirred and sodium carbonate (50 mL, 2.5 M) was added to the mixture following with addition of sodium hydroxide (3 M) until pH 10. Reaction was kept at 70 °C for 24 hours to form solid material. Solid material was filtered, washed with water several times, and dried at 110 °C.

2.3 Preparation of $K_4[\alpha\text{-}SiW_{12}O_{40}]$

Synthesis of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was conducted using mixing of sodium tungstate (182 g in 300 mL hot water) with hydrochloric acid (4 M, 165 mL). This hydrochloric acid was added very slowly with gentle stirring. Sodium metasilicate (11g, 100 mL water) was added to the reaction mixture following addition of hydrochloric acid (4 M, 50 mL). The pH of solution was kept at 5 by addition hydrochloric acid for one hour. Sodium tungstate (1 M, 80 mL) was added quickly after one hour to the solution. The solution was cooled at room temperature and potassium chloride (50 g) was pour into mixing solution to form solid material of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ as similar reported by Legagneux et al., [23].

2.4 Intercalation Zn-Cr LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$

Intercalation of Zn-Cr LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$ ion was conducted by ion exchange method as previous reported by Palapa et al., [24]. Polyoxometalate of $K_4[\alpha\text{-}SiW_{12}O_{40}]$ (1 g in 50 mL water) was added with Zn-Cr LDH (2 g in 25 mL sodium hydroxide). The mixing solution was stirred under nitrogen atmosphere for 24 hours. The obtained material washed and dried at 110 °C overnight.

2.5 pH PZC Analysis

The analysis of pH pzc (point zero charge) was conducted using various pH solutions of sodium hydroxide or hydrochloric acid into solution of sodium chloride 0.1 M. The pH medium of sodium chloride was adjusted to range 1-10 by addition of hydrochloric acid 0.1 M or sodium hydroxide 0.1 M solutions. Zn-Cr LDH and intercalated Zn-Cr LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion was added to the series pH solution of sodium chloride. The solution mixtures were constantly stirred for 24 hours. The solutions were filtered, and pH of the filtrate was determined by pH meter. The graph of pHpzc was obtained by comparison initial and final pH solution.

2.6 Adsorption Study

Adsorption of cobalt(II) on Zn-Cr LDH and intercalated Zn-Cr LDH was performed at pH pzc value. The factors that influencing adsorption were studied such as adsorption time, initial concentration of cobalt(II), and temperature adsorption. The performance of adsorbent was evaluated by

regeneration process. The effect of adsorption time was studied in the range 5-150 minutes. Initial concentration of cobalt(II) was studied in the range 10-30 mg/L at temperature 30-60 °C. Regeneration of adsorbent was performed after desorption process. Desorption was conducted using various solvents such as hydrochloride acid, water, hot water, sodium hydroxide, hydroxylamine chloride, and sodium EDTA. The optimum results of desorption were used for regeneration process. Regeneration was conducted until three cycles adsorption process using similar adsorbent.

3. RESULTS AND DISCUSSION

The analysis results of X-Ray analysis of Zn-Cr and intercalated materials are shown in Figure 1. Zn-Cr LDH has diffraction peaks at 11.74° (003), 23.49° (006), 34.33° (009), 39.26° (012), and 60.41° (110). The diffraction peaks at 11.74° (003) and 60.41° (110) are unique due to well-known layer structure formation in these areas [25]. On the other hand, the interlayer distance of Zn-Cr LDH was formed with a gallery of 7.53Å. Intercalation of Zn-Cr LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$ ion formed Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDH. The diffraction peaks of Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ were shown in Figure 1B.

The diffraction peaks of Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ were appeared at 8.62°, 23.39°, 34.23°, and 60.88°. The diffraction at 8.62° is the interlayer distance of LDH after intercalation and has gallery 10.35 Å. The gallery distance is increased 2.82 Å after intercalation of Zn-Cr LDH with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion.

Figure 2 shows FTIR spectrum of Zn-Cr and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDHs. Vibration peak of Zn-Cr LDH was appeared at wavenumber 3446/cm (υ O-H stretching), 1643/cm (υ O-H bending), 1381/cm (υ N-O nitrate), and 841/cm (υ Cr-O), and 339/cm (υ Zn-O). Zn-Cr LDH after intercalation has FTIR spectrum as shown in Figure 2B. There are some vibration peaks of Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ at 3425/cm, 1635/cm, 1381/cm, 879/cm, and 360/cm [18]. The vibration peak at 1381/cm after intercalation is sharp due to ion exchange process of nitrate to polyoxometalate ion $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$. Nitrate ion is not fully exchanged with polyoxometalate ion probably due to size of $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$ is large than all available space on interlayer gallery of Zn-Cr LDH.

The nitrogen adsorption-desorption on Zn-Cr and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ were shown in Figure 3. There is a hysteresis loop of adsorption-desorption

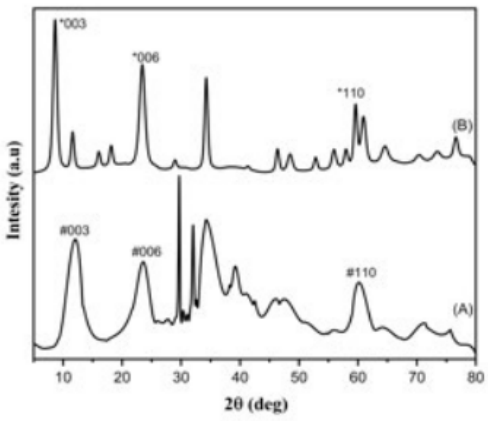

Figure 1. X-Ray Diffraction patterns of Zn-Cr LDH (A), Zn-Cr LDH intercalated with $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$ (B).

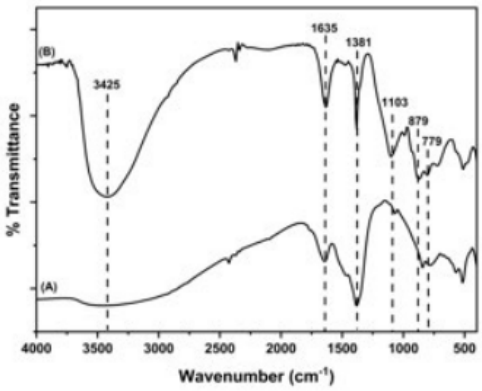

Figure 2. FTIR spectra of Zn-Cr LDH (A), Zn-Cr LDH intercalated with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (B).

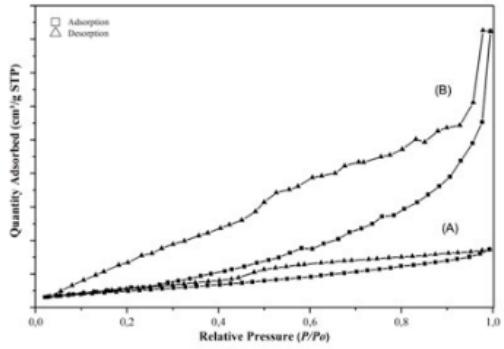

Figure 3. N_2 adsorption-desorption profile of Zn-Cr (A), Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ (B).

Table 1. Physical properties of materials.

LDH Materials	Surface area (m^2/g)	Pore volume (BJH) (cm^3/g)	Pore diameter (BJH) (nm)
Zn-Cr	31.638	0.063	3.934
Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$	128.871	0.163	3.695

curves on both materials. The adsorption curve has a different shape with desorption curve due to irregular pore and shape on Zn-Cr and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDHs [26]. The surface area, pore volume, and pore diameter properties were obtained from Figure 3 and the data was shown in Table 1.

The physical properties of Zn-Cr modified to form Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ has four-fold larger than before intercalation process. The insertion

of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion on interlayer distance of Zn-Cr LDH not only increase the interlayer gallery but also surface area of material. Besides, the pore diameter of Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ is lower than pristine material due to irregular shape of Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ after intercalation.

The pH pzc of Zn-Cr and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDHs is presented in Figure 4. The pH pzc is the state of material, where the charge is zero. The point below than pH pzc means the materials have positive charge and vice versa [27]. Material Zn-Cr LDH has intersection point at 7.5 and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ at 8. Thus, at that point is pH pzc of Zn-Cr and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDHs and charge of material is zero. The pH pzc was used to conduct adsorption. First process of adsorption was studied through the effect of adsorption time as shown in Figure 5.

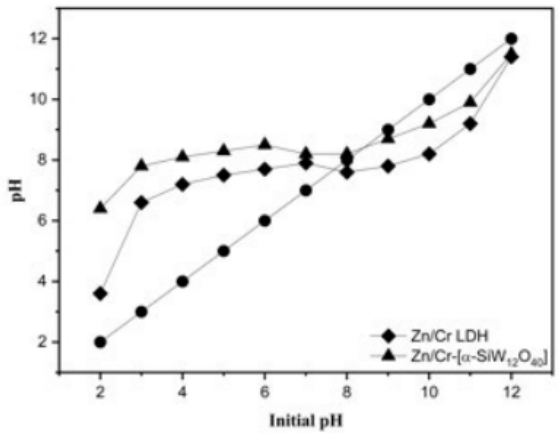

Figure 4. pH PZC analysis of Zn-Cr LDH and Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$.

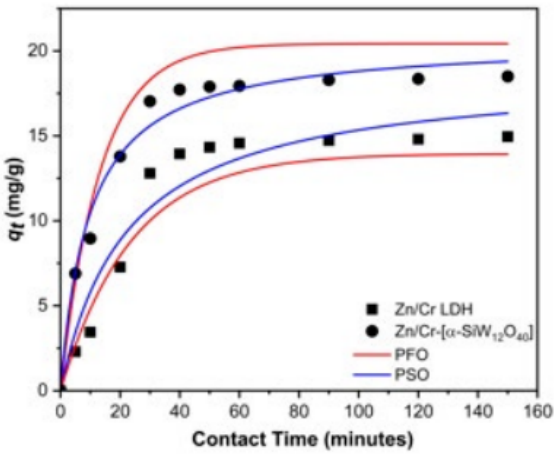

Figure 5. Effect of adsorption time of cobalt(II) on Zn-Cr (A), Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]^{4}$ (B).

Adsorption process of cobalt(II) on Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] LDHs as shown in Figure 5 was gradually increased with increasing adsorption time and reach equilibrium at more than 100 minutes adsorption time. The data in Figure 5 is also showed that Zn-Cr-[α-$SiW_{12}O_{40}$] more good adsorbed cobalt(II) than Zn-Cr LDH. These data in Figure 5 is used to obtain kinetic parameter data for cobalt(II) adsorption on Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] using pseudo-first-order and pseudo-second-order kinetic model as written as previous research [22].

The data in table 2 showed that adsorption of cobalt(II) on Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] follow PSO rather than PFO due to R^2 value is closed to one. The k_2 value for Zn-Cr LDH is 0.033 g/mg.min lower than Zn-Cr-[α-$SiW_{12}O_{40}$] LDH (0.052 g/mg.min). The reactivity of Zn-Cr-[α-$SiW_{12}O_{40}$] LDH is higher than Zn-Cr LDH due to opening layer of Zn-Cr-[α-$SiW_{12}O_{40}$] after intercalation and material is to reactive than pristine material. Thus, Table 2 also showed the qe calc and qe exp for PSO is closed and higher than PFO equation. This finding also related that PSO is better described the kinetic adsorption process of cobalt (II) using Zn-Cr LDH and Zn-Cr-[α-$SiW_{12}O_{40}$].

The effect of initial concentration of cobalt(II) and temperature adsorption on Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] LDH was shown in Figure 6.

Both adsorbents in Figure 6 have similar adsorption patterns. The amount of cobalt(II) adsorption on both adsorbents increased with increasing initial concentration of cobalt(II). The increasing adsorption temperature was also increased the amount of cobalt(II) adsorbed on materials. The data in Figure 6 was calculated to obtain Langmuir and Freundlich isotherms adsorption using equation according to [28] . The results were shown in Table 3.

The Freundlich isotherm is suitable for Zn-Cr LDH rather than Langmuir isotherm and R^2 value is 0.999. On the other hand, Zn-Cr-[α-$SiW_{12}O_{40}$] follow Langmuir isotherm model. The Qmax of Zn-Cr-[α-$SiW_{12}O_{40}$] has adsorption capacity 45.45 mg/L at 303 K and that value is higher than Zn-Cr LDH with adsorption capacity 30.39 mg/L at 303 K. Thus, kF was denotes the favorable interact between adsorbent and adsorbate [29]. The kF value of Zn-Cr-[α-$SiW_{12}O_{40}$] is <14.5 at high temperature. This finding indicated that the adsorption process was favorable at room temperature. The thermodynamic adsorption parameter was also obtained from data in Figure 6, and the results were listed in Table 4. The value of ΔG is negative of both adsorbents indicated that adsorption of cobalt(II) on Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] is spontaneously occurred. The ΔS value is in the range 17.628-38.865 kJ/mol for Zn-Cr LDH and 18.634-64.452 kJ/mol for

Table 2. Kinetic adsorption model for removal of cobalt(II).

Metal Ion	Kinetic Model	Parameter	Zn-Cr	Zn-Cr[α-$SiW_{12}O_{40}$]
Co(II)	PFO	q_e exp (mg/g)	16.797	19.556
		q_e calc (mg/g)	3.314	2.464
		k_1 (min^{-1})	0.043	0.049
		R^2	0.976	0.986
	PSO	q_e exp(mg/g)	16.797	19.556
		q_e calc (mg/g)	17.064	19.762
		k_2 (g/mg.min)	0.033	0.052
		R^2	0.999	0.999

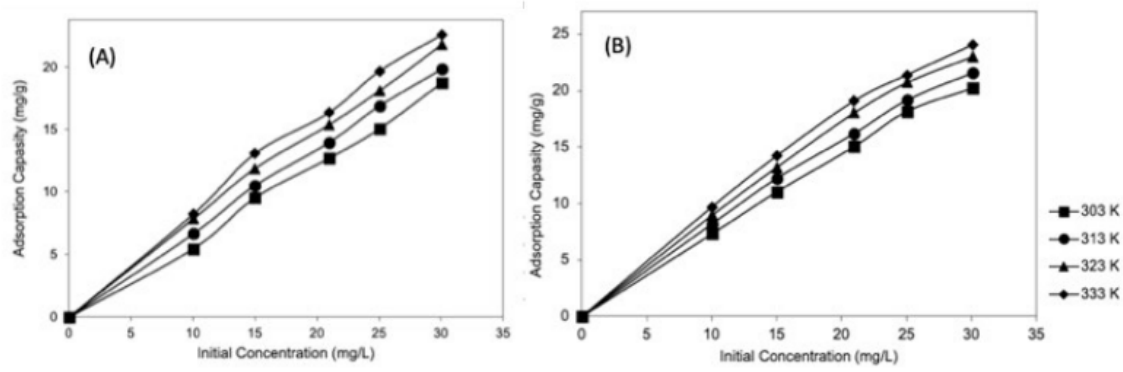

Figure 6. Effect of initial concentration of cobalt(II) and temperature on Zn-Cr LDH (A), Zn-Cr LDH intercalated with $[\alpha\text{-}SiW_{12}O_{40}]^{4+}$ (B).

Table 3. Isotherm adsorption for removal of cobalt(II).

LDH	Isotherm Adsorption	Adsorption Constant	T (K)			
			303	313	323	333
Zn-Cr	Langmuir	Qmax	30.39	44.516	44.05	29.76
		kL	0.033	0.044	0.099	0.398
		R^2	0.995	0.999	0.995	0.995
	Freundlich	n	0.753	1.294	1.389	2.515
		kF	1.374	3.312	4.479	10.123
		R^2	0.998	0.999	0.999	0.999
Zn-Cr-[α-$SiW_{12}O_{40}$]	Langmuir	Qmax	45.45	38.023	31.64	24.51
		kL	0.082	0.160	0.406	1.838
		R^2	0.994	0.978	0.992	0.999
	Freundlich	n	1.509	1.595	1.983	2.982
		kF	4.491	5.994	9.465	14.595
		R^2	0.993	0.973	0.947	0.973

Zn-Cr-[α-$SiW_{12}O_{40}$] LDH. These findings also related to Langmuir isotherm adsorption was belongs to chemical sorption. On the other hand, the randomness adsorption system increased after intercalation process.

Table 5 showed the comparison of adsorption capacity from cobalt (II) removal using several adsorbents. The results showed that the higher adsorption capacity of cobalt (II) was obtained by Zn-Cr-[α-$SiW_{12}O_{40}$]. This finding confirmed that LDH modified has good ability to remove cobalt (II) from wastewater.

The performance of Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] LDHs as adsorbents of cobalt(II) was evaluated by adsorption regeneration process. Prior that procedure, the desorption was conducted using several reagents as shown in Figure 7. Hydrochloric acid solution and hot water are suitable reagents

Table 4. Thermodynamic adsorption.

Co(II) (mg/L)	T (K)	Qe (mg/g)		ΔH (kJ/mol)		ΔS (kJ/mol)		ΔG (kJ/mol)	
		ZnCr	Zn-Cr-[α-$SiW_{12}O_{40}$]	ZnCr	Zn-Cr-[α-$SiW_{12}O_{40}$]	ZnCr	Zn-Cr-[α-$SiW_{12}O_{40}$]	ZnCr	Zn-Cr-[α-$SiW_{12}O_{40}$]
10,02	303	5.471	7.310	38.865	64.452	0.130	0.203	-0.527	-2.980
	313	8.192	3.819					-1.827	0.951
	323	8.958	3.970					-3.127	-1.078
	333	9.686	4.156					-4.427	-3.107
15,00	303	9.533	11.027	38.454	50.940	0.131	0.176	-1.182	-2.302
	313	10.529	12.215					-2.490	-4.059
	323	11.908	13.211					-3.799	-5.817
	333	13.096	14.207					-5.107	-7.574
20,98	303	12.713	15.05	23.638	39.347	0.081	0.137	-1.052	-2.136
	313	13.977	16.199					-1.867	-3.505
	323	15.395	18.038					-2.682	-4.874
	333	16.352	19.073					-3.497	-6.243
25,04	303	15.05	18.153	24.381	23.211	0.084	0.084	-1.017	-2.381
	313	16.889	19.149					-1.855	-3.226
	323	18.115	20.72					-2.694	-4.070
	333	19.686	21.372					-3.532	-4.915
30,10	303	18.766	20.222	17.628	18.634	0.025	0.067	-1.232	-1.785
	313	19.877	21.563					-1.854	-2.459
	323	21.831	23.019					-2.477	-3.133
	333	22.598	24.015					-3.099	-3.807

Table 5. Comparison adsorption capacity of several adsorbents.

Adsorbent	Qmax (mg/g)	References
Pine sawdust	1.11	[14]
lemon peel biomass	22	[30]
SiAl zeolite	12.4	[10]
Coal fly ash	4.01	[15]
MgAl LDH	36.8	[16]
CaAl LDH	21	[16]
Silica Gel modified rice husk ash	12.3	[31]
MgAl LDH	1.15	[12]
Zn-Cr-[α-$SiW_{12}O_{40}$]	45.45	This research
Zn-Cr LDH	30.39	This research

to desorb cobalt(II) on both adsorbents. Probably the involvement of acid base reaction between cobalt(II) and both adsorbents is occurred in the adsorption. Regeneration process was conducted after desorption of cobalt(II) on Zn-Cr and Zn-Cr-[α-$SiW_{12}O_{40}$] LDHs using hydrochloric acid following with washing using hot water and dried at 110 °C. The adsorption was conducted for three cycles adsorption process using similar adsorbent after desorption. The results are shown in Figure 8.

Figure 8 showed that cycling adsorbent will decrease the adsorption of cobalt(II). The adsorption ability is sharply decreased after three cycles process regeneration. These phenomena are due to sprayed and exfoliated process on LDH [32]. That is frequently occurred on all LDH but this research showed that intercalation process using $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ will increased surface area properties and adsorption capacity of cobalt(II) on LDH.

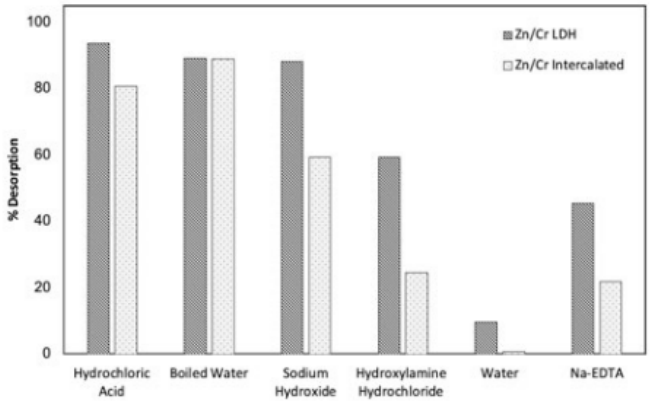

Figure 7. Desorption of cobalt(II) on Zn-Cr LDH (A), Zn-Cr LDH intercalated with [α-$SiW_{12}O_{40}$]$^{4-}$ (B).

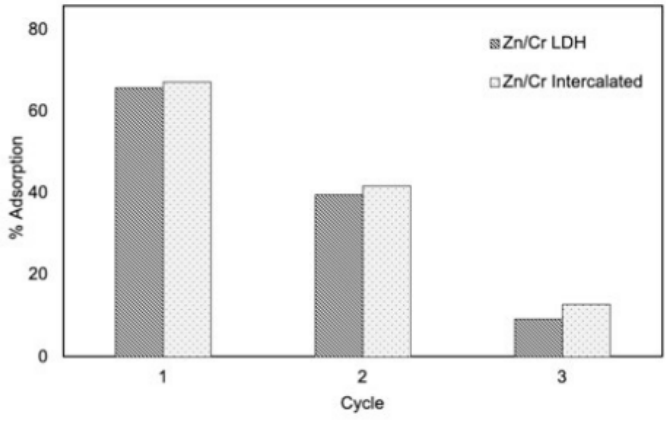

Figure 8. Regeneration study of adsorbent Zn-Cr LDH (A), Zn-Cr LDH intercalated with [α-$SiW_{12}O_{40}$]$^{4-}$ (B).

4. CONCLUSIONS

The interlayer gallery of Zn-Cr was increased after intercalation of $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ ion from 7.53Å to 10.35Å. The surface area of Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDH (128.871 m^2/g) was also higher than Zn-Cr LDH (31.638 m^2/g). Adsorption of cobalt (II) was conducted at pH 7.5 on Zn-Cr LDH and pH 8 on Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$. Adsorption of cobalt(II) on both adsorbents follow pseudo second order kinetic model with k_2 Zn-Cr-$[\alpha\text{-}SiW_{12}O_{40}]$ LDH higher than k_2 Zn-Cr LDH. Adsorption of cobalt(II) on LDHs was spontaneous, increasing the randomness and classify as physical adsorption. Regeneration of adsorbent three times will decrease the ability of adsorbent to adsorb cobalt(II) from aqueous solution.

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CONFLICT OF INTEREST STATEMENT

The author declares that there is no conflict of interests regarding the publication of this manuscript.

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