

ORIGINAL ARTICLE

Adsorption of Cr(VI) Using the Adsorbent of Hydroxyapatite Extracted from Bali Bovine Bone Waste and Coated with Fe-Al Oxides

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ABSTRACT

In this research, the adsorbent of hydroxyapatite (HA) extracted from bali bovine bone waste was coated with Fe-Al oxides, characterized and then applied to adsorb Cr(VI). To produce Fe-Al oxide coated HA adsorbent, the hydroxyapatite was activated using 0.4 M NaOH and coated with Fe-Al-hydration ion agents with mass ratios of HA and Fe-Al oxide respectively 10:1; 20:1 and 100:1, and then calcinated to form active sites of Fe-Al oxides. The results showed that the adsorbent of Fe-Al oxide coated HA had higher surface acidity, formed new Lewis acid sites, enhanced BET surface area, increased BJH porosity (pore radius, pore volume, and micropore volume), as well as the amount of Fe-Al oxides coated into HA structure compared to the Fe-oxide coated HA and uncoated HA. The highest surface acidity was obtained by using the mass ratio of HA and Fe-Al oxide of 10:1. The average pore radius was less than 29.09 nm. In the adsorption isotherm, the adsorbent of Fe-Al oxide coated HA significantly increased its adsorption ability and followed the Freundlich model that assumed the multilayer adsorption over its heterogenous surface.

Keywords: Hydroxyapatite, bali bovine bone, Fe-Al oxide coated, Cr(VI), adsorption

Received 24.08.2018 Accepted 02.10.2018

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INTRODUCTION

Hexavalent chromium [Cr(VI)] is a metal anion that is more toxic and difficult for handling than Cr(III) [1; 2]. Sources of chromium can be derived from waste of chrome electroplating, the dominant toxic metal containing Cr(VI). In addition, the dyeing waste also contains Cr(III) and Cr(VI) above the threshold. According to World Health Organization, the maximum level of total chromium in drinking water is 0.05 mg/L [3]. When consumed by human beings, it can cause gastrointestinal irritation until the organ damage, cyanosis and skin irritation as well as produce cancer agent [4]. Moreover, it can be toxic to lungs, cause kidney damage, enzyme inactivation and when exposed to the skin it can cause skin damage and cancer [1].

Recently, activated carbon has been most commonly used for reducing the content of metal waste, but it is so costly, has relatively low selectivity level of adsorption and difficult to be regenerated so that has been encouraging the importance to obtain other materials for replacement [5]. One interesting material to be used as an alternative is bali bovine bone obtained from handicraft waste, an organic material containing predominantly hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] bio-mineral which has porous structure and inert, so that it could potentially be used as an adsorbent which is recyclable, environmentally friendly and renewable as well as easy to obtain and inexpensive [6; 7]. Laperche *et al.* (1996) have reported that the synthetic mineral of hydroxyapatite can be used to adsorb toxic metals of Pb(II) which contaminated the soil [8]. Chen *et al.* (1997) have also mentioned that the synthetic mineral of hydroxyapatite can be used as adsorbent for toxic metals of Pb, Cd, and Zn [9]. Donadel *et al.* (2009) have synthesized hydroxyapatite chemically, coated with Fe₂O₃ through a dry spray technique, to produce medical products [10]. However, the three studies were mentioned by using synthetic mineral of hydroxyapatite, not taking the advantage of natural hydroxyapatite, hence relatively more expensive as well as non-renewable and non-biodegradable.

Although bovine bone is potentially applied as an adsorbent, but without any modifications the adsorption has a limited performance, because of the pores are covered with the organic and inorganic impurities as well as its active sites are minimal. The determining factors of the adsorption are specific

surface area, porosity, and active sites. These weaknesses could be overcome through the extraction of hydroxyapatite from the bone and then coated with Fe-Al oxides, which produced higher activity of adsorbent with pore size of 1-100 nm (nano-pores) and having more active sites [11]. Besides, Fe and Al are relatively cheap metals, easy to obtain, and also safe for the environment [10]. Satpathy and Chaudhuri (1997) modified the natural sand with coating Fe_2O_3 to be used as adsorbents for cadmium (Cd) and chromium (Cr) [12]. The result showed that Fe_2O_3 coated sand had a specific surface area and larger pore size ($1.59 \text{ m}^2/\text{g}$) than without coating Fe_2O_3 ($0.04 \text{ m}^2/\text{g}$), because the folds were formed only into the pores of the sand and therefore creating new active sites of Fe oxides. The similar model has also been done by Simpfen *et al.*, 2012, through the use of Fe_2O_3 coated sand as an adsorbent for nitrate ions [13]. It has been reported that it increased the nitrate ions adsorption capacity of 2.83 mg/g compared to without Fe_2O_3 coated.

This study aimed to extract hydroxyapatite (HA) from Bali bovine bone waste by using alkaline hydrothermal and thermal decomposition, then coated with Fe-Al oxide, characterized, and applied to adsorb Cr(VI) in the solution. The characterization included surface acidity, functional groups, BET surface area, BJH porosity, and the amount of coated Fe-Al into HA.

MATERIALS AND METHODS

Materials

Powder of Bali bovine bone waste was obtained from Tampak Siring Gianyar Bali; Whatman filter papers 42; standard solutions of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) 1000 mg/L (atomic absorption spectrometric grade) diluted with deionized water; sodium hypochloride (NaOCl); sodium hydroxide (NaOH); hydrogen peroxide (H_2O_2), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were reagent grade diluted with distilled water. Other chemicals were also reagent grade.

Methods

Coating hydroxyapatite with Fe-Al oxide

Four hundred (400) g of hydroxyapatite (HA) prepared using Wahl and Czernuszka (2006) procedure [6] and modified by Simpfen and Suastuti (2016) [11] was put into a Beaker glass, added with 0.4 M NaOH solution with a ratio of 1:1.5, and then heated at 60-65°C, stirred using a magnetic stirrer for 2.5 hours to produce activated HA. The mixture was filtered and the residue washed repeatedly with distilled water until free from alkaline (negative test using phenolphthalein). The residue then dried in the oven at 105-110°C until the weight was constant. Into three 250 mL Beaker glasses, each filled with 100 g of activated HA and then added with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with mass ratio of 10:1, 20:1, and 100:1 respectively. Afterward, the mixtures were diluted with distilled water with ratio of 22:5 for 2 minutes, then immediately calcined at 200°C for 5 hours [11; 12]. The samples were labeled as HA₁-Fe-oxide, HA₂-Fe-oxide, and HA₃-Fe-oxide. Into three 100 mL Beaker glasses, respectively filled with 50 g HA₁-Fe-oxide, HA₂-Fe-oxide, and HA₃-Fe-oxide and then added with $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ with mass ratios of 10:1, 20:1, and 100:1. The mixtures diluted with distilled water with ratio of 22:5, and after interaction for 2 minutes immediately calcined at 350°C for 12 hours [11]. Furthermore, the samples were labeled as HA₁-Fe-Al-oxide, HA₂-Fe-Al-oxide, and HA₃-Fe-Al-oxide. The samples were analyzed for their surface acidities by using acid-base titration, functional groups by using Fourier transform infrared spectroscopy (FTIR, Shimadzu/IR Prestige-21), surface areas by using the Brunauer, Emmett and Teller (BET) and Barret, Joyner and Halenda (BJH) porosities by using gasorption nitrogen analyzer (Quantacrome instruments version 2.0). Meanwhile, the amount of coated Fe-Al in the adsorbent was analyzed by using laser induced breakdown spectroscopy (LIBS, Ocean optics, USA/insight).

Optimization of contact time

The amount of 0.3 g of adsorbent (which had the highest surface acidity and BET surface area) was added with 25.0 mL of Cr(VI) 75 mg/L. Afterward, the mixture was stirred by a magnetic stirrer for 5, 10, 15, 30, 60, 120, and 150 minutes. The mixture then filtered using Whatman filter paper 42. Furthermore, the amount of Cr(VI) was determined by atomic absorption spectrophotometer (AAS, Shimadzu/AA-7000 series). From these experiments, the optimum time of Cr(VI) adsorption for each adsorbent could be determined.

Adsorption isotherms and adsorption capacity

Into seven of 100 mL Erlenmeyer flasks respectively filled with 0.3 g of adsorbents of HA, HA₁-Fe-oxide, HA₂-Fe-oxide, HA₃-Fe-oxide, HA₁-Fe-Al-oxide, HA₂-Fe-Al-oxide, and HA₃-Fe-Al-oxide. Each flask added with 25.0 mL of Cr(VI) with concentrations of 10, 25, 50, 75, 100, and 150 mg/L, then allowed to react during the optimum time by stirring the solution with a magnetic stirrer. Subsequently, filtered by Whatman filter paper 42 and the content of Cr(VI) in the filtrate was analyzed by AAS at the wavelength

(λ) of 357.87 nm. By knowing the amount of Cr(VI) remaining, the amount of adsorbed Cr(VI) could be calculated using the equation below:

$$q_{ads} = \frac{(C_0 - C_e)V}{m} = q_e \quad \dots 1$$

Where, C_0 and C_e are the initial concentration of Cr(VI) and at the equilibrium (mg/L), V is the volume of the solution (L), q_{ads} is the amount of adsorbed Cr(VI) (mg) in unit mass of adsorbent (g), so that the adsorption capacity (mg of Cr(VI)/g of adsorbent) can be calculated [14-16]. Afterward, from the extrapolation of the adsorption isotherm models of Langmuir and Freundlich [16; 17], the adsorption capacity of the adsorbent can be determined. Langmuir adsorption isotherm model is measured by plotting $\frac{C_e}{q_{ads}}$ versus C_e , while Freundlich adsorption isotherm model by plotting $\log q_{ads}$ versus $\log C_e$.

Which model is more applicable determined by the straight line in the graph [15]. Furthermore, as a comparator to the adsorption of Cr(VI) was also conducted using HA.

RESULTS AND DISCUSSION

The characteristics of adsorbents

The result of intensity of coated Fe and Al in HA and surface acidity of the adsorbents were summarised in Table 1.

Table 1: The LIBS analysis and surface acidity of adsorbents without and with Fe oxide and Fe-Al oxide coateds

Adsorbents	Intensity of Fe (a.u)	Intensity of Al (a.u)	Surface acidity (mmol/g)
HA	23.67	0	0.0588
HA ₁ -Fe-oxide	208.67	0	0.3219
HA ₂ -Fe-oxide	175.67	0	0.2258
HA ₃ -Fe-oxide	132.67	0	0.1065
HA ₁ -Fe-Al-oxide	208.67	47.00	0.5097
HA ₂ -Fe-Al-oxide	175.67	35.00	0.3594
HA ₃ -Fe-Al-oxide	132.67	18.33	0.1933

Table 1 showed that the correlation between the ratio of Fe and Al coated in HA and the intensity of Fe and Al coating was positive linear. This indicated that the amount of coated Fe and Al into HA increased as the mass ratio of Fe and Al also increased, showing that the coating has highly entered into the crystal structure of HA. According to Kumar *et al.* (2008), increasing the initial Fe concentration for the coating was synergistic to the increasing of Fe-loading on the surface [18]. Further, based on the X-ray diffractogram, the Fe-loading completely formed crystals with a sharp peak and the maximum intensity.

The surface acidity of Fe-oxide coated HA and Fe-Al oxide coated HA adsorbents was higher than surface acidity of uncoated HA. This means that the coating could increase the surface acidity of the adsorbents. The highest value was obtained with Fe-Al oxide coated HA (HA₁-Fe-Al-oxide) with ratio of HA and Fe-Al oxide of 10:1. When the ratio of HA and Fe-Al oxide was low, the value of surface acidity was higher. Similar to the coated HA with Fe oxide, the less amount of Fe the less value of surface acidity. It showed that Fe and Al provided higher surface acidity and especially created more Lewis acid sites. These were further supported by the previous study by Simpffen and Suastuti (2016) proving that new Lewis acid sites (P-O-Fe and P-O-Fe-Al) were formed by coating HA with Fe oxide and Fe-Al oxide [11].

The distribution of Bronsted acid sites and Lewis acid sites after adsorbing ammonia vapor was characterised based on FTIR analysis. Ammonia vapor sorption aimed to strengthen the appearance of functional groups of Bronsted acid sites at the wave numbers of 1300-1550 cm^{-1} and Lewis acid sites at 1650-1700 cm^{-1} [7; 11]. The FTIR spectra for the distribution of acid sites showed that the adsorbent of HA only had Bronsted acid sites (PO₂H), while the adsorbents of HA-Fe-oxide and HA-Fe-Al-oxide had Bronsted and Lewis acid sites (P-O-Fe and P-O-Fe-Al). This indicated that coating Fe-oxide and Fe-Al-oxide formed Lewis acid sites [11].

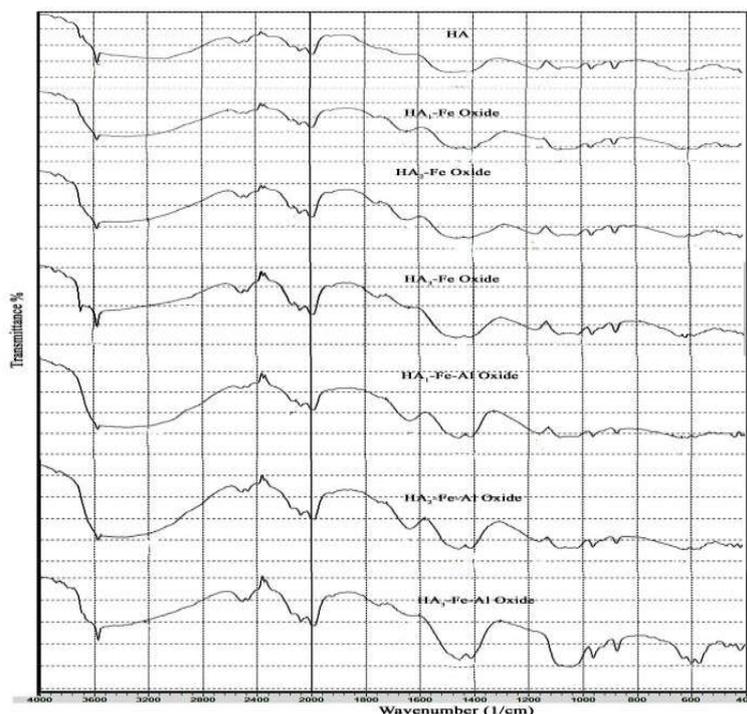


Fig. 1: FTIR spectra of adsorbents without and with Fe oxide and Fe-Al oxide coatings

The FTIR spectra (Fig. 1), it could be seen that the adsorbent of uncoated HA had the absorption peaks at 588, 640, 1161, and 1471 cm^{-1} attributed as phosphate (PO_4^{3-}) and 1415 cm^{-1} as carbonate (CO_3^{2-}). The peak at 3072 cm^{-1} corresponded to the -OH stretching vibration of adsorbed water, while small peaks at 3570 cm^{-1} attributed as the stretching of the -OH ion lattice [16; 19]. Meanwhile, adsorbent of HA-Fe-Al-oxide showed absorption peaks at 1151 and 1452 cm^{-1} which were attributed as the phosphate (PO_4^{3-}), 1411 cm^{-1} as carbonate (CO_3^{2-}), and 1641 cm^{-1} as P-O-Fe-Al.

Table 2: Specific surface area and porosity of the adsorbents without and with Fe oxide and Fe-Al oxide coatings

Adsorbents	BET surface area (m^2/g)	BJH pore radius (nm)	BJH pore volume ($\times 10^{-1}$) (cm^3/g)	BJH mikropore volume ($\times 10^{-1}$) (cm^3/g)
HA	2.49	1.53	0.24	0.00
HA ₁ -Fe-oxide	9.12	1.71	0.89	0.06
HA ₂ -Fe-oxide	5.70	9.47	0.68	0.03
HA ₃ -Fe-oxide	5.13	16.91	0.88	0.02
HA ₁ -Fe-Al-oxide	4.04	1.53	0.58	0.04
HA ₂ -Fe-Al-oxide	4.67	1.54	0.55	0.04
HA ₃ -Fe-Al-oxide	7.51	29.09	1.18	0.01

The specific surface area (BET surface area) data in Table 2, it indicated that the coating process increased the specific surface area compared to uncoated HA. The highest number (9.12 m^2/g) was obtained from the adsorbent of Fe-oxide-coated HA with ratio 10:1 (HA₁-Fe-oxide). Furthermore, by increasing ratio of Al added in the adsorbents of HA-Fe-oxide decreasing the BET surface area of HA-Fe-Al-oxide adsorbents. Moreover, higher amount of Fe or Al decreased the pore radius, but the volume of micropores was increase. This showed that the coating formed new pore folds, so that micropores were formed [20].

Optimization of contact time

In Fig. 2, both adsorbents of HA₁-Fe-oxide and HA₁-Fe-Al-oxide (based on the highest surface acidity and BET surface area) had the highest concentration of adsorbed Cr(VI) at the contact time of 60 minutes, which were 3.6802 mg/g for HA₁-Fe-oxide and 3.3156 mg/g for HA₁-Fe-Al-oxide, so that the contact time

of 60 minutes was selected to measure the adsorption isotherm for all the adsorbents. Therefore, the contact time of 60 minutes was determined as the equilibrium time of adsorption.

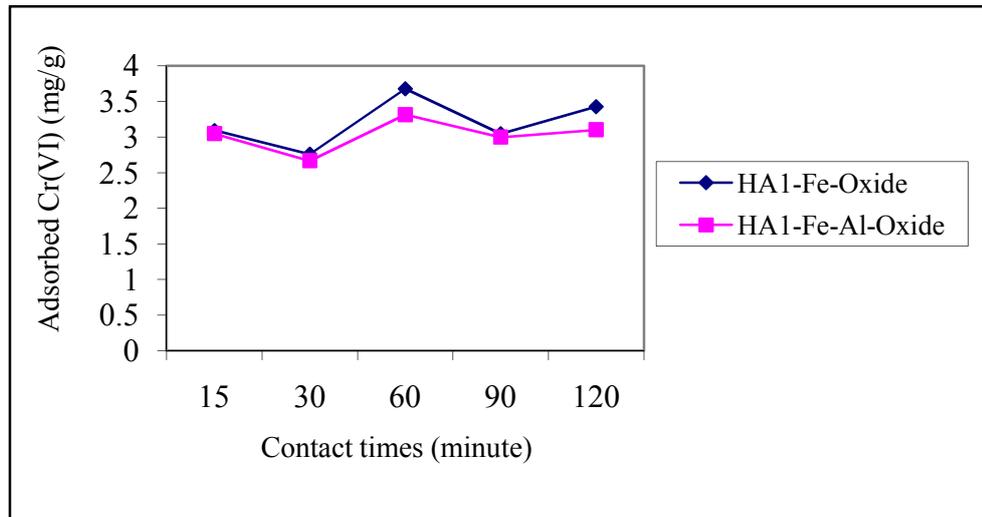


Fig. 2: The effect of contact time to the amount of absorbed Cr(VI)

Adsorption isotherms and adsorption capacity

For all the coated HA adsorbents, it was found that increasing the initial concentrations of Cr(VI) caused the increase of adsorbed Cr(VI) at higher capacity than uncoated HA for all concentrations (Fig. 3). Adsorbents of HA-Fe-oxide and HA-Fe-Al-oxide produced higher concentration of adsorbed Cr(VI) compared to uncoated HA adsorbent starting from the initial concentration of 25 mg/L. It was predominantly determined by BET surface area, pore radius, and pore volume. This phenomenon was consistent with the research by Kongsri *et al.* (2013), which found that increasing the capacity of the adsorption equilibrium (q_e) of hydroxyapatite adsorbents from fish bones and commercial hydroxyapatite was accordance with the increase of concentration of adsorbed tetravalent selenium [Se(IV)], but it was unlike the case for chitosan adsorbent when the initial concentration was high it would decrease the q_e (at the adsorption equilibrium) [16]. This was influenced by a combination of high pore volume, pore diameter, and specific surface area. Those models were the same as the research result by Simpen and Suastuti (2016) which showed that the amount of adsorbed methylene blue (MB) by hydroxyapatite adsorbent increased with the increase of initial MB concentration [11].

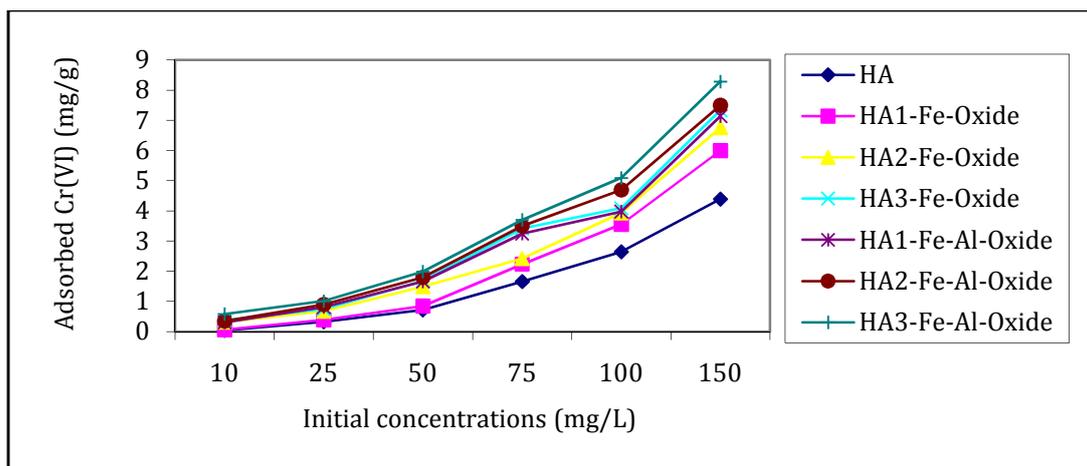


Fig. 3: The effect of initial concentration to the amount of adsorbed Cr(VI)

The Langmuir adsorption isotherm is represented by the following linear equation below and presented in Table 3:

$$\frac{C_e}{q_{ads}} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots 2$$

Where, K_L is the Langmuir constant (L/mg) and q_m is the maximum amount of adsorbed Cr(VI) on the adsorbent (mg/g). The Freundlich isotherm equation is represented as linearity by the following equation and presented in Table 3:

$$\log q_{ads} = \log K_F + \frac{1}{n} \log C_e \dots 3$$

Where, K_F is the Freundlich constant (mg/g) and n is the intensity adsorption factor [21; 22]. The value of $\frac{1}{n}$ imply the type of isotherm and can be classified as irreversible ($\frac{1}{n} = 0$), favorable ($0 < \frac{1}{n} < 1$), and unfavorable ($\frac{1}{n} > 1$) [23; 24].

Table 3: The Langmuir and Freundlich adsorption isotherms and adsorption capacity of Cr(VI)

Adsorbents	Langmuir Isotherm		Freundlich Isotherm		
	q_m (mg/g)	R^2	K_F (mg/g)	1/n	R^2
HA	4.8010	0.5628	1.6223	0.3896	0.9861
HA ₁ -Fe-oxide	5.6171	0.6751	2.2842	0.5357	0.9782
HA ₂ -Fe-oxide	10.3562	0.6679	2.5999	0.4287	0.9482
HA ₃ -Fe-oxide	11.6094	0.4398	2.9120	0.4023	0.9301
HA ₁ -Fe-Al-oxide	5.7761	0.7172	2.7889	0.6981	0.9752
HA ₂ -Fe-Al-oxide	10.5309	0.6893	3.0988	0.6626	0.9741
HA ₃ -Fe-Al-oxide	12.1780	0.0383	3.5013	0.4555	0.8693

Table 3 showed that the adsorption isotherm followed the model of Freundlich isotherm with correlation coefficient (R^2) more than 0.86. It means that is based on the adsorption of adsorbate Cr(VI) on a heterogeneous surface of adsorbent and relies on the physical interaction [23]. Based on these values, the highest adsorption capacity of the Cr(VI) solution was obtained by using HA₃-Fe-Al-oxide adsorbent (3.5013 mg/g). Meanwhile, the HA₃-Fe-oxide adsorbent produced less adsorption capacity (2.9120 mg/g), whereas HA adsorbent (uncoated) provided the smallest value (1.6223 mg/g). This indicated that the coating on HA adsorbent could significantly improve the adsorption ability of Cr(VI). However, based on the value of 1/n, the strength of bond between the Cr(VI) solute with the adsorbent of HA₃-Fe-Al-oxide was relatively weak (0.4555), but provided an indication of the favorability of adsorption [23]. The 1/n value correlated with the surface acidity, where the highest value of 1/n was obtained by the highest surface acidity of adsorbent.

CONCLUSION

In conclusion, the adsorbent of hydroxyapatite (HA) coated with Fe-Al-oxide produced higher surface acidity, formed new Lewis acid sites, enhanced BET surface area, increased BJH porosity (pore radius, pore volume and micropore volume), compared to uncoated HA and the HA coated with Fe-oxide. The coating of Fe-oxide and Fe-Al-oxide on hydroxyapatite which is extracted from Bali bovine bone waste could improve their characteristics. They were increased the adsorption ability to adsorb Cr(VI) from the solution and following the adsorption isotherm model of Freundlich ($R^2 > 0.86$) as a heterogeneous surface of adsorbent and relies on the physical interaction. The adsorption capacity of HA-Fe-Al-oxide and HA-Fe-oxide adsorbents were 3.5013 mg/g and 2.9120 mg/g, whereas HA was the smallest (1.6223 mg/g).

ACKNOWLEDGEMENTS

We would like to thank to the Research Directorate and Community Service of Kemristekdikti Indonesia through the Research and Community Service of Udayana University for financial support in Competitive Grants of Decentralization.

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CITE THIS ARTICLE

I Nengah Simpén, N.G.A.M. Dwi Adhi Suastuti², IM. Sutha Negara and Oka Ratnayani. Adsorption of Cr(VI) Using the Adsorbent of Hydroxyapatite Extracted from Bali Bovine Bone Waste and Coated with Fe-Al Oxides. *Res. J. Chem. Env. Sci.* Vol 6[5] October 2018. 23-29