

## Evaluation of Lagergren Kinetics Equation by Using Novel Kinetics Expression of Sorption of $Zn^{2+}$ onto Horse Dung Humic Acid (HD-HA)

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### ABSTRACT

Extraction and purification of humic acid from dry horse dung powder (HD-HA) was performed successfully and the purified HD-HA was then applied as sorbent to adsorb  $Zn^{2+}$ . Extraction and purification were performed based on procedure of Stevenson (1994) under atmospheric air. Parameters investigated in this work consist of effect of medium sorption acidity, sorption rate ( $k_a$ ) and desorption rate constant ( $k_d$ ), Langmuir (monolayer) and Freundlich (multilayer) sorption capacities, and energy ( $E$ ) of sorption. The  $k_a$  and  $k_d$  were determined according to the kinetic model of second order sorption reaching equilibrium, monolayer sorption capacity ( $b$ ) and energy ( $E$ ) were determined according to Langmuir isotherm model, and multilayer sorption capacity ( $B$ ) was determined based on Freundlich isotherm model. Sorption of  $Zn^{2+}$  on purified HD-HA was maximum at pH 5.0. The novel kinetic expression resulted from proposed kinetic model has been shown to be more applicable than the commonly known Lagergren equation obtained from the pseudo-first order sorption model. The application of the equation revealed that the intercept of Lagergren equation,  $\ln q_e$  was more complex function of initial concentration of  $Zn^{2+}$  ( $a$ ), Langmuir sorption capacity ( $b$ ), and sorbed  $Zn^{2+}$  at equilibrium ( $x_e$ ).

**Keywords:** Lagergren kinetics equation; novel kinetics expression; sorption;  $Zn^{2+}$ ; horse dung humic acid (HD-HA)

### ABSTRAK

Ekstraksi dan pemurnian asam humat dari serbuk tinja kuda kering (HD-HA) telah dilakukan dengan baik dan HD-HA yang telah dimurnikan kemudian digunakan sebagai adsorben untuk mengadsorpsi  $Zn^{2+}$ . Ekstraksi dan pemurnian dilakukan berdasarkan prosedur Stevenson (1994) di bawah atmosfer udara. Parameter-parameter yang diamati dari penelitian ini terdiri dari pengaruh medium keasaman adsorpsi, tetapan laju adsorpsi ( $k_a$ ) dan tetapan laju desorpsi ( $k_d$ ), kapasitas adsorpsi Langmuir (lapis tunggal) dan Freundlich (lapis banyak) dan energi adsorpsi ( $E$ ). Nilai  $k_a$  dan  $k_d$  ditentukan menurut model kinetika orde dua ketika adsorpsi mencapai kesetimbangan. Nilai kapasitas adsorpsi lapis tunggal Langmuir dan lapis banyak Freundlich ditentukan berdasarkan model isoterm Langmuir dan Freundlich. Adsorpsi  $Zn^{2+}$  pada HD-HA yang telah dimurnikan berlangsung maksimal pada pH 5,0. Persamaan kinetika baru yang diusulkan menunjukkan bahwa persamaan ini lebih aplikatif daripada persamaan pseudo orde satu Lagergren. Penerapan persamaan ini pada adsorpsi mengungkap bahwa intersep dari persamaan garis Lagergren,  $\ln q_e$  merupakan fungsi yang lebih kompleks dari konsentrasi awal  $Zn^{2+}$  ( $a$ ), kapasitas adsorpsi Langmuir ( $b$ ) dan  $Zn^{2+}$  teradsorpsi pada kesetimbangan ( $x_e$ ).

**Kata Kunci:** persamaan kinetika Lagergren; persamaan kinetika baru; sorpsi;  $Zn^{2+}$ ; asam humat tinja kuda (HD-HA)

### INTRODUCTION

The levels of metals on waters have been seriously increased during the last few decades due to human activities [1]. Several methods have been developed to reduce metal in waste, such as adsorption, electrolysis, dialysis, complexation, ion exchange, solvent extraction, and some kind of membrane separation techniques [2-10]. Adsorption still become preferred method for reducing heavy metal in aquatic environment because it is simple and gives satisfactory result [11]. Many efforts done by experts today are looking for new sources of

sorbent that had high performance and derived from renewable source. Some of them, has been reported such as fly ash, nut shell, activated carbon, rice husk, rice husk ash, wheat bran, coconut shell, coconut shell charcoal, tamarind seeds activated carbon, calcite, humic acid [12-20]. Humic acid is reported to have widely used to reduce or eliminate metals in surface water, such as Zn(II), Pb(II), Cr(III), Ni(II), Cd(II), Cu(II), and rare earth elements [21-27]. Unfortunately, humic acid usually extracted from peat soil. Peat soil as a source of humic acid has less green aspect, because it can't be renewed immediately. In addition, exploitation

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of peat land potentially releases stored carbon in the soil, so it can contribute to increasing the greenhouse effect [28]. One source of humic acid that has been reported is cow dung. Cow dung can be a source of humic acid which is greener, cheap, and still have good sorption ability [29-31].

Based on this report, it is possible that other animal's dung, like a horse that has texture and properties similar to cow dung can also be used as a source of humic acid. Horse dung has a denser and rough texture from cow dung, so it is rarely used for biogas and organic fertilizer. The existence of horse dung often cause bad affect for environment because the dung is scattered so it cause smell and the appearance of nuisance animals that come from the dung. If the horse dung can be a source of humic acid, its treatment not only solves the environmental problems caused by waste horse dung, but also it's giving advantage in waste heavy metal handling in the environments. Based on the green properties of horse dung compared to peat as a source of humic acid, it is interesting to extract and study the kinetics and thermodynamics sorption of horse dung humic acid to adsorb  $Zn^{2+}$  metal ions.

The study of kinetic sorption was according to developed kinetics model based on an approach that sorption is a dynamic equilibrium process and during mathematical derivation the availability of binding sites of sorbent. The applicability of the developed sorption kinetic model is then tested for the sorption of  $Zn^{2+}$ , where their distribution in soil and water has been known to be strongly associated with the presence of humic substance [32]. The evaluation is carried out for the determination of  $k_a$  of the sorption of  $Zn^{2+}$  on HD-HA. The sorption kinetic model is also evaluated for Lagergren kinetic model [33-37], especially the value of its intercept ( $\ln q_e$ ) often found not equal between  $\ln q_e$  from Lagergren equation and value of  $\ln q_e$  from experiment [38]. Furthermore, comparison of developed kinetics model to the most widely used Lagergren pseudo first-order also critically discussed.

## EXPERIMENTAL SECTION

### Materials

All reagent are analytical grade i.e. NaOH, HCl, HF,  $AgNO_3$ ,  $Ba(OH)_2$ ,  $Ca(CH_3COO)_2 \cdot H_2O$ ,  $Cd(CH_3COO)_2 \cdot 2H_2O$ ,  $Zn(CH_3COO)_2 \cdot 2H_2O$  from Merck Co. Inc (Germany) and used without further purification. Humic acid is extracted from horse dung dried for  $\pm 3$  months from Saddle horse aged 7 months to 4 years old from Bantul, Special Region of Yogyakarta and peat soil was taken from Musi Banyuasin, South Sumatra as comparator. Extraction was performed according to the

procedure of Stevenson [39] under atmospheric air. Purification was done by HCl/HF method [39].

### Instrumentation

These work used Hanna Instrument Portable pH Meter, magnetic stirrer, glassware, and Jena ContraAAS 300 Atomic Absorption Spectroscopy (AAS) to analyze total metal ions in sample. The characterization of horse dung humic acid (HD-HA) and peat soil humic acid (PS-HA) was performed by Shimadzu FTIR Prestige 21 and UV-visible spectrophotometer (GBC Cintra 2020).

### Procedure

#### Effect of medium acidity

At first, a series of 50 mL of Zn(II) was prepared and their acidity was adjusted to 2.0, 3.0, 4.0, 5.0, and 6.0 by adding HCl solution. Into every Zn(II) solution, 10 mg of purified HD-HA was poured and then stirred for 2 h. After filtering through 100 mesh membrane filter, the concentration of Zn(II) in supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under same conditions. The amount of sorbed  $Zn^{2+}$  was considered to be the difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed.

AAS is a specific for elemental analysis, especially for metals. Its main components consist of a light source, atomization unit, a prism to disperse and isolate the emission lines, and a detector with appropriate amplifiers [40]. The light source with wavelength readily absorbed by the element to be determined is directed through the atomization unit, which maybe either flame or flameless apparatus. A measure of intensity is made without the sample and then with the sample introduced into the atomization unit. The decrease in intensity observed with the sample is a measure of the concentration of the element.

#### Sorption capacity and energy

The thermodynamic experiments were carried out using a batch type reactor using 50 mL Erlenmeyer in a water bath at  $25 \pm 0.01$  °C. As much as 10 mg of sorbents was interact with and stirred in 50 mL of solutions containing the various concentrations of 5, 10, 20, 30, 40, 50, 100, 200, and 400 mg/L of  $Zn^{2+}$  at pH 5.0 for 2 h and then aged for 24 h. After separating the supernatants, the concentration  $Zn^{2+}$  in the supernatant was determined by AAS. Under the same condition with the sample solution, the blank solution was also analyzed. The data obtained was then

analyzed using Freundlich and Langmuir isotherm models.

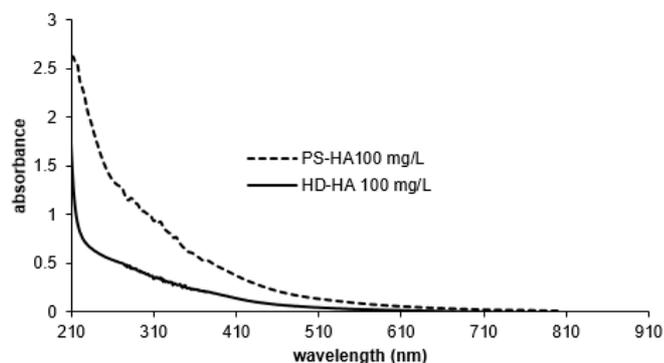
### Sorption kinetics

The kinetics experiments also were carried out using a batch type reactor using 50 mL Erlenmeyer in a water bath at  $25 \pm 0.01$  °C. The volume of sorption medium was 50 mL, the initial metal ion concentration was 50, 200, and 400 mg/L, the acidity was adjusted at pH 5.0; and to each solutions, 10 mg of sorbent was added and then stirred continuously. At selected interaction time, the sample was immediately filtered through 100 mesh filter and the concentration of  $Zn^{2+}$  in the supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under the same conditions. The amount of  $Zn^{2+}$  sorbed was considered to be difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed. The data obtained was then analyzed by two different sorption kinetics models, i.e. Lagergren pseudo-first order and the proposed kinetics expression here.

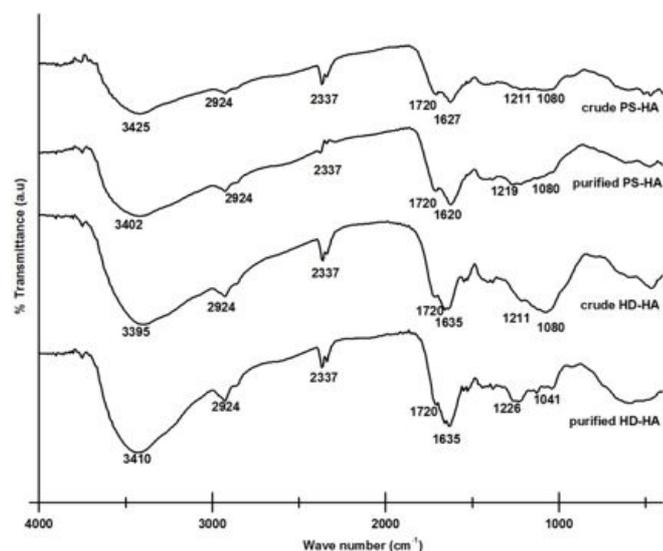
## RESULT AND DISCUSSION

### Characterization of HD-HA

Horse dung humic acid (HD-HA) has the physical appearance and texture similar with peat soil humic acid (PS-HA), which was dark brown. UV-Vis characteristic spectra of humic acid do not indicate a maximum or a minimum peak clear where the highest absorbance in the UV region, then decreases with increasing wavelength. These results were similar to studies conducted by Stevenson [39] and Agarwal, et al. [41]. The high absorbance in the region 250-300 nm was characteristic of aromatic group or unsaturated compound which is a chromophore group of double bonds (C=C, C=O, and C=N) (Fig. 1). It was also showed a high concentration of aromatic compounds and humification degree of humic acid [42]. UV-Vis spectra of humic compounds are widely used to determine the molecular properties of humic compounds [43]. There are three important areas where absorbance must be measured, i.e. about 280 nm, 400-500 nm and above 600 nm. Absorbance ratio can be calculated on the  $A_{280}/A_{472} = Q_{2/4}$ ,  $A_{280}/A_{664} = Q_{2/6}$ , and  $A_{472}/A_{664} = Q_{4/6}$ . Based on this ratio, degree of maturity (humification) of organic matter can be determined.  $Q_{2/4}$  shows the proportion of lignin and other materials at the beginning of the process of humification [44],  $Q_{2/6}$  indicate the proportion between material humified and unhumified. The low value of  $Q_{2/6}$  and  $Q_{4/6}$  showed a high degree of aromatic and degree of humification of organic material [45].  $Q_{4/6}$  was used to measure degree of condensation and polymerization of aromatic compounds



**Fig 1.** UV-VIS spectra of HD-HA compared to PS-HA shows the similar pattern and give the characteristics pattern of humic acid



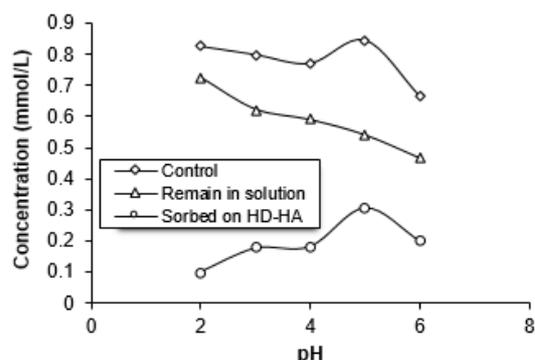
**Fig 2.** FT-IR spectra of crude and purified HD-HA compared to crude and purified PS-HA shows the similar peaks and gives the characteristics peaks of humic acid

and can serve as humification index [46]. The ratio of  $Q_{2/4}$ ,  $Q_{2/6}$ , and  $Q_{4/6}$  of peat soil humic acid (PS-HA) and HD-HA were 34.99; 5.60; 6.25 and 41.94; 6.28; 6.68, respectively. Ratio  $Q_{4/6}$  for humic acid is  $<5$ , while fulvic acid is between 6 and 8.5 [39]. HD-HA has a ratio  $Q_{4/6}$  close to 5 which shows the characteristics of the humified material but not perfect. While the HD-HA has a ratio  $Q_{4/6}$  in the area of fulvic acid is 6.275. This indicates that HD-HA has not been humified perfectly. These results are consistent with the fact that the horse dung has been used in this research only about 3 months old at depths less than 50 cm in the open areas.

The characterization of HD-HA using Fourier transform infra red (FT-IR) spectroscopy shown that their peaks were similar to PS-HA as a comparator which is

**Table 1.** Sorption capacity ( $b$ ), energy ( $E$ ), and constant of equilibrium ( $K$ ) obtained from Langmuir isotherm as well as sorption capacity ( $B$ ) obtained from Freundlich isotherm for the sorption of  $Zn^{2+}$ 

	Sorption parameters						
	$b$ ( $10^{-3}$ mol $g^{-1}$ )	$K$ (mol/L) $^{-1}$	$E^a$ (kJ/mol)	$R^2$	$B$ ( $10^{-2}$ mol $g^{-1}$ )	$n$	$R^2$
Langmuir	1.070	6.399	21.858	0.992	-	-	-
Freundlich	-	-	-	-	6.912	1.827	0.983

<sup>a</sup> $E=RT \ln K$ **Fig 3.** Effect of medium acidity on the distribution of  $Zn^{2+}$  in the presence of HD-HA

have characteristics peak of humic acid [39]. Humic acid usually give a wide absorption band in  $3300-3400\text{ cm}^{-1}$  which indicate H-bonds of O-H group (Fig. 2). Absorption at  $2940-2900\text{ cm}^{-1}$  region indicates the stretching of C-H aliphatic. Absorption at  $1725-1720\text{ cm}^{-1}$  region indicate C=O stretching -COOH. In a certain cases, it was found a new peak at  $1550$  and  $1400\text{ cm}^{-1}$  which indicate carboxylate ion absorption ( $COO^-$ ). This evidence shows that the C=O group at humic acid still interact with something like metal-clay because it has not been purified. Small peak at  $1720\text{ cm}^{-1}$  is an open chain ketone or residual aldehyde, as was the case in this study. Sharp peak was also often found in the area in  $2330$  which is the C=O stretching vibration of  $CO_2$  trapped in the matrix KBr from decarboxylation results of COOH groups. Absorption at  $1625-1620\text{ cm}^{-1}$  region indicate C=C aromatic and aromatic rings formed by hydrogen bonding OH group and C=O groups quinones. Peak in the region  $1280-1200\text{ cm}^{-1}$  indicate O-H bending and C-O stretching from COOH. The fifth area of this absorption ( $3400, 2900, 1720, 1600,$  and  $1200\text{ cm}^{-1}$ ) is characteristic for humic acid [39].

Purification process aims to eliminate inorganic impurities such as clay minerals and silicates [39]. The yield of ash level for crude PS-HA, purified PS-HA, crude HD-HA, and purified HD-HA were 7.31; 1.2; 15.66 and 0.99 (% w/w), respectively. The successfulness of purification process was indicated by the results of ash level of PS-HA and HD-HA after purification process was lower than before purification process. This result confirmed by decreasing absorption of FT-IR spectra in a finger print region of silica-alumina ( $1080\text{ cm}^{-1}$ ). The

successfulness of purification process was also indicated by increasing in total acidity. Total acidity in this work was determined by Barium Hydroxide (Baryta Absorption) Method [39]. Total acidity of crude HD-HA and purified HD-HA were 400.6 and 415.3 cmol/kg, respectively. FT-IR spectra before and after purification process showed a significant differences in the functional groups of humic acid. After purification there is an increase in the intensity of the main absorption of humic acid functional group which explains the presence of these groups in the sample. The group which was increase in the intensity was O-H absorption at wave number  $3400\text{ cm}^{-1}$  and C-O absorption at wave number  $1226\text{ cm}^{-1}$  in purified HD-HA. Changes in the FT-IR spectra, ash level, and total of acidity show that purified HD-HA has fewer impurities.

### Effect of Medium Acidity

The acidity of the sorption medium greatly affects of the amount sorbed  $Zn^{2+}$  (Fig. 3). In the absence of sorbent, nearly all  $Zn^{2+}$  existed in the soluble form at  $pH \leq 5.0$  and began precipitated at  $pH > 6.0$  (theoretical pH of  $Zn^{2+}$  began precipitated was  $\geq 8.5$  [47]). In the presence of sorbent, the sorption of  $Zn^{2+}$  increased with increasing pH from 2 to 5. From pH 8 to lower acidity the sorption significantly decreased. The increase of sorption from pH 2 to 5 may be caused by the decrease of the amount of  $H^+$  in the medium, therefore, the competition between  $H^+$  and  $Zn^{2+}$  in occupying the active site on the sorbent also decreased. At pH higher than 5, the sorption compete with the precipitation (form  $Zn(OH)_2$ ) and other species has been formed ( $Zn(OH)^+$ ) [48]. As a result, the maximum sorption of  $Zn^{2+}$  occurred just at the medium acidity in which has not been formed other species of Zn(II) and in which  $Zn^{2+}$  started precipitating.

### Sorption Capacity and Energy

Determination of capacity and sorption energy of  $Zn^{2+}$  on sorbent (HD-HA) was plotted using Langmuir and Freundlich isotherm models. Langmuir isotherm model:  $C/m = 1/b K + C/b$ . Freundlich isotherm model:  $\ln m = \ln B + 1/n \ln C$ , where  $C$ , the equilibrium concentration in solution;  $b$ , Langmuir's sorption capacity;  $K$ , Langmuir's constant of equilibrium;  $m$ , metal

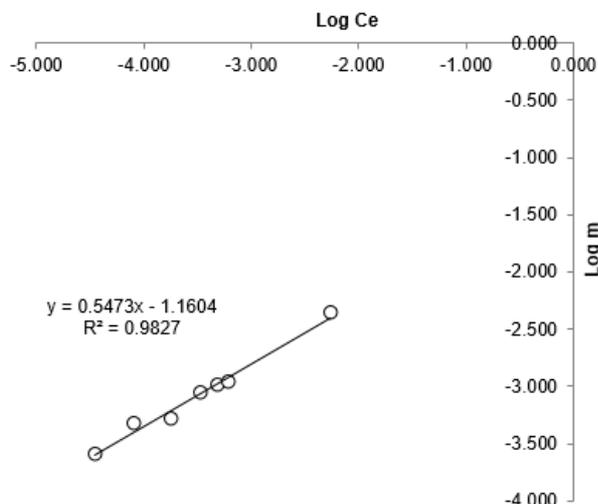


Fig 4. Freundlich isotherm sorption of  $Zn^{2+}$  onto HD-HA

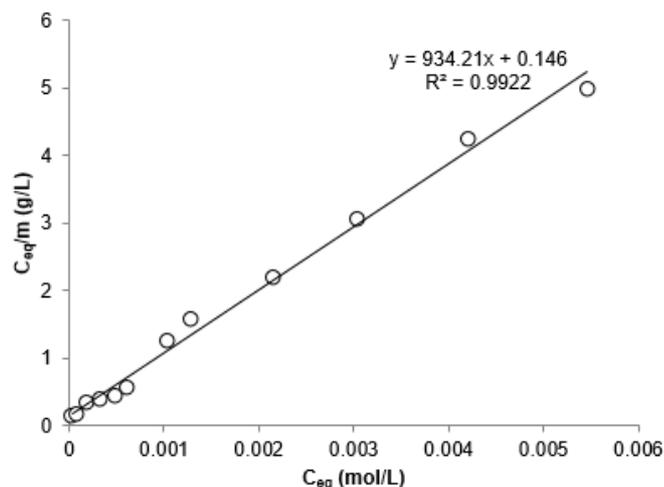


Fig 5. Langmuir isotherm sorption of  $Zn^{2+}$  onto HD-HA

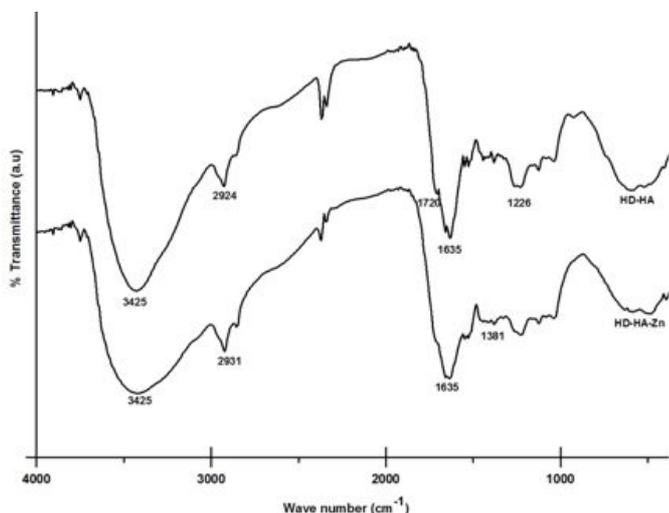


Fig 6. FT-IR spectra of HD-HA before and after sorbing  $Zn^{2+}$  sorption

sorbed per gram sorbent at equilibrium;  $B$ , Freundlich isotherm capacity and  $n$ , constants.

If it is assumed that sorption follows the Langmuir isotherm model, the sorption capacity ( $b$ ) and constant of equilibrium ( $K$ ) can be calculated respectively from the slope and intercept of plot between  $C/m$  and  $C$ . If it is assumed that sorption follows the Freundlich isotherm model, the sorption capacity ( $B$ ) can be obtained from the intercept of plot between  $\ln m$  versus  $\ln C$ . The application of the two models was resulted the sorption parameters shown in Table 1. Compared to the Freundlich model (Fig. 4), the experimental data appeared to match better in Langmuir isotherm model (Fig. 5). The plot of Langmuir model yielded better linearity ( $R^2 = 0.992$ ) than Freundlich model ( $R^2 = 0.983$ ). The sorption capacity of HD-HA for  $Zn^{2+}$

obtained in this study i.e.,  $1.070 \times 10^{-3} \text{ mol g}^{-1}$ , or equivalent to  $69.978 \text{ mg g}^{-1}$ .

The Langmuir isotherm is designed for monolayer sorption of species on a homogeneous surface with the same sorption energy for all active site regardless of the degree of coverage, while the Freundlich is for multilayer sorption on heterogeneous surface with the frequency of sites associated with free energy of sorption decrease exponentially with the increase of free energy [25]. Humic acid has many active side as  $O^-$  (enolate),  $-COOH$  (carboxylic),  $-NH$  (amide),  $-O-$  (ether),  $C=O$  (carbonyl), etc. Among the active side, the oxygen containing functional groups such as  $-O-$  and  $-COO^-$  is the most reactive functional groups [39]. FT-IR studies showed that  $-COO^-$  plays an important role in metal complexation [39]. If we assume  $-COO^-$  is the responsible group for the adsorption of metal ions, then the capacity (monolayer or mono-energy) Langmuir adsorption may indicate the number of this group. It was proved by Langmuir has better linearity than Freundlich Linearity. Because metal ions will occupy the active site that has the strongest interaction occupies first and then the active side with lower energy. While capacity (multilayer or multi-energy) indicates the Freundlich adsorption capacity  $-COO^-$  and all active side together. Interactions were occurred allegedly as electrostatic forces between the metal ions with active sites of horse dung humic acid. FT-IR spectra can provide little information about the electrostatic interaction between sorbate and sorbent (Fig. 6). The weakening of the  $C=O$  absorption of  $-COOH$  on wave number  $1720 \text{ cm}^{-1}$  after interaction with  $Zn^{2+}$  indicates the interaction of  $C=O$  group on the sorbent with  $Zn^{2+}$ .

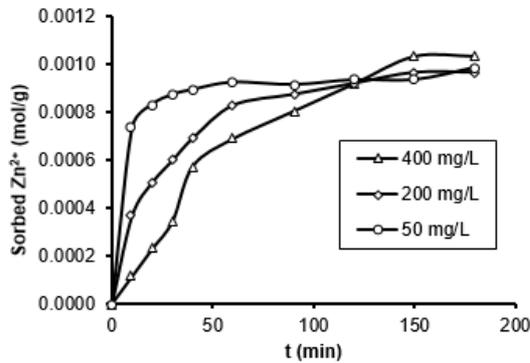


Fig 7. Sorption profile of various concentrations of  $Zn^{2+}$  onto HD-HA as a function of interaction time

### Sorption Kinetics

The sorption profile of HD-HA as a function of time interaction is presented in Fig. 7. The sorption of  $Zn^{2+}$  50 mg/L is initially rapid and then goes slower. The initial rapid sorption was observed for the first 45 min and then goes slower after 60 min. After 120 min, it is relative no additional  $Zn^{2+}$  adsorbed on HD-HA, so it can be argued that the sorption has reached equilibrium.

Considering the sorption of  $Zn^{2+}$  on sorbent is an equilibrium process as illustrated below:



where  $A$  is a metal  $Zn^{2+}$ ;  $S$  is an sorbent (HD-HA);  $k_a$  is the sorption rate constant and  $k_d$  desorption rate constant.

If  $a$  is the initial concentration of metal  $A$  (mol/L),  $b$  is the Langmuir sorption capacity (mol/L) and  $x$  is the number of  $A$  is adsorbed on the  $S$  (mol/L), so the equation rate can be written:

$$r_{ads} = \frac{dx}{dt} = k_a(a-x)(b-x) - k_d x \quad (1)$$

At equilibrium,  $\frac{dx}{dt} = 0$ , so

$$k_d = \frac{k_a(a-x_e)(b-x_e)}{x_e} \quad (2)$$

Substituting eq. (2) into eq. (1) yields

$$\frac{dx}{dt} = k_a(a-x)(b-x) - \frac{k_a(a-x_e)(b-x_e)}{x_e} x \quad (3)$$

It can be simplified in a simple form

$$\frac{dx}{(ab-x_e x)(x_e-x)} = \frac{k_a}{x_e} dt \quad (4)$$

At time = 0, sorption has not happen yet so  $k_a$  is 0 and metal ion of  $A$  has not adsorbed on sorbent  $S$ , so  $x = 0$ . Taking integration for the eq. (4) with limit  $(ab)$  to  $(ab-x_e x)$ , 0 to  $(x)$ , and 0 to  $t$ , so eq. (4) can be written

$$\frac{x_e}{(x_e^2-ab)} \int_{ab}^{ab-x_e x} \frac{1}{ab-x_e x} dx + \frac{1}{(ab-x_e^2)} \int_0^x \frac{1}{(x_e-x)} dx = \frac{k_a}{x_e} \int_0^t dt \quad (5)$$

Integration of eq. (5) results

$$\ln \left( \frac{(ab-x_e x)x_e}{(x_e-x)ab} \right) = k_a \frac{ab-x_e^2}{x_e} t \quad (6)$$

Rearranged eq. (6) gives

$$\ln \left( \frac{ab-x_e x}{x_e-x} \right) = k_a \left( \frac{ab-x_e^2}{x_e} \right) t - \ln \left( \frac{x_e}{ab} \right) \quad (7)$$

Or

$$\ln(x_e-x) = \ln \left( \frac{x_e(ab-x_e x)}{ab} \right) - k_a \left( \frac{ab-x_e^2}{x_e} \right) t \quad (8)$$

The eq. (8) is surprisingly the same as Lagergren equation,  $\ln(q_e - q) = \ln(q_e) - k_{lag} t$ , where  $q_e$  and  $x_e$  has the same unit (mol/L). Thus allegedly linearity of eq. (7) will be similar to the linearity Lagergren pseudo-first order. The same plot between eq. (8) with a Lagergren pseudo-first-order model is  $\ln(x_e-x)$  versus  $t$  will generate relationships,  $k_{lag} = k_a ((ab-x_e^2)/x_e)$ . If the eq. (8) give a straight line, the intercept  $\ln q_e$  from Lagergren has a value equal to  $\ln(x_e(ab-x_e^2)/ab)$  and answered questions of Aharoni and Sparks [38] why the parameter  $\ln q_e$  always have different values with  $\ln q_e$  obtained from experimental data.

Lagergren kinetics equation assume that sorbat concentration ( $a$ ) is in excess rather than adsorption capacity ( $b$ ), so from eq. (1) if  $a$  assumed to be in excess,  $a \gg x, (a-x) \cong a$ , eq. (1) can be rewritten:

$$\frac{dx}{dt} = k_a' a(b-x) - k_d x \quad (9)$$

At equilibrium  $\frac{dx}{dt} = 0$ , so

$$k_d = \frac{k_a' a(b-x_e)}{x_e} \quad (10)$$

Substituting eq. (10) into eq. (9) yields

$$\frac{dx}{dt} = \frac{k_a'}{x_e} ((b-x)x_e - (b-x_e)x) \quad (11)$$

It can be simplified to be a simple form

$$\frac{dx}{(x_e-x)} = \frac{k_a' ab}{x_e} dt \quad (12)$$

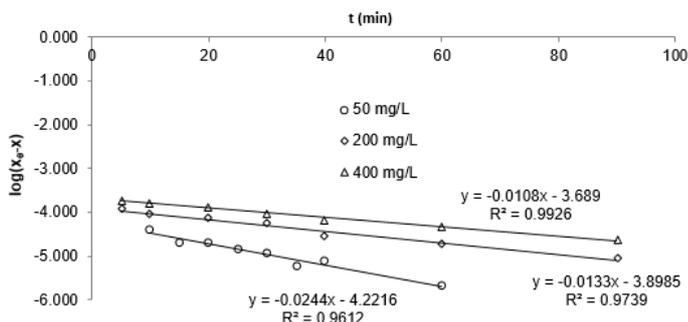
At time = 0, sorption has not happen yet so  $k_a$  is 0 and metal ion of  $A$  has not adsorbed on sorbent  $S$ , so  $x = 0$ . Taking integration for the eq. (12) with limit 0 to  $(x)$ , and 0 to  $t$ , so eq. (12) can be written

$$\int_0^x \frac{dx}{(x_e-x)} = \frac{k_a' ab}{x_e} \int_0^t dt \quad (13)$$

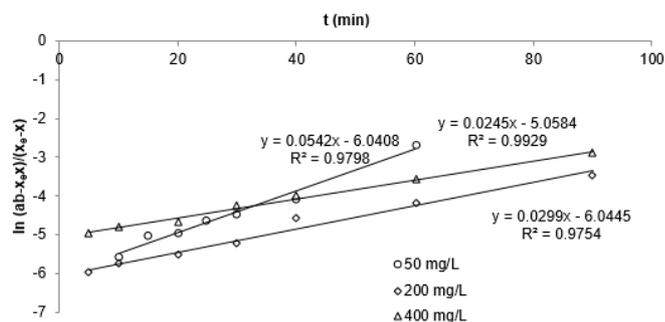
Integration results and rearranged gives

$$\ln(x_e-x) = \ln x_e - k_a' \frac{ab}{x_e} t \quad (14)$$

If assumption  $a \gg b$  is right, value of  $k_a'$  in eq. (14) will closer to  $k_a$  when concentration of  $a$  much higher than  $b$ . To verify equations above, in our study it has



**Fig 8.** Plot  $\ln(x_e-x)$  vs.  $t$  or  $\ln(q_e-q_t)$  vs  $t$  from Lagergren kinetics equation at various concentrations of  $Zn^{2+}$  onto HD-HA



**Fig 9.** Plot  $\ln((ab-x_e x)/(x_e-x))$  vs.  $t$  from eq. (7) at various concentrations of  $Zn^{2+}$  onto HD-HA

**Table 2.** Linearity ( $R^2$ ) and rate constant of Lagergren pseudo-first order ( $k_{lag}$ ), proposed kinetics expression ( $k_a$ ), and proposed kinetics expression assuming  $a \gg b$  ( $k_a'$ ), and for the sorption of various concentration  $Zn^{2+}$  on HD-HA

[ $Zn^{2+}$ ] (a) ( $\times 10^{-4}$ mol/L)	Lagergren kinetics equation			Proposed kinetics expression			
	$R^2$	$k_{lag}$ $10^{-2}$ $\text{min}^{-1}$	$\ln q_e$	$R^2$	$k_a$ $\text{min}^{-1}$ (mol/L) $^{-1}$	$k_a'$ $\text{min}^{-1}$ (mol/L) $^{-1}$	$\ln((x_e(ab-x_e^2))/ab)$
$a_1$	0.9612	5.619	-1.833	0.9798	73.21	60.63	-1.662
$a_2$	0.9711	2.971	-1.693	0.9754	19.81	18.04	-1.637
$a_3$	0.9926	2.487	-1.606	0.9929	3.995	3.92	-1.606

been done time variation for concentration of  $Zn^{2+}$  i.e.  $a_1$ ,  $a_2$ , and  $a_3$  are 50 mg/L ( $8.075 \times 10^{-4}$  mol/L), 200 mg/L ( $14.81 \times 10^{-4}$  mol/L) and 400 mg/L ( $61.11 \times 10^{-4}$  mol/L), respectively. The parameters of kinetics model can be seen in Table 2. Plot  $\ln(x_e-x)$  vs.  $t$  or  $\ln(q_e-q_t)$  vs  $t$  onto Lagergren model (Fig. 8) showed higher linearity at the increasingly excessive concentration of  $Zn^{2+}$ . The value of  $R^2$  from plot  $\ln((ab-x_e x)/(x_e-x))$  vs.  $t$  in eq. (7) has similarity to the Lagergren model, this indicate the both kinetics model is suitable in the same optimum condition (Fig. 9).

When the concentration of  $Zn^{2+}$  increased from 8.07 to  $61.11 \times 10^{-4}$  mol/L, the value of  $k_{lag}$  was also changed from 0.05619 to  $0.02487 \text{ min}^{-1}$ . The same thing was also shown by the eq. (7) change from 73.210 to  $3.995 \text{ min}^{-1} (\text{mol/L})^{-1}$ . Although the adsorption is done on the isotherm condition,  $k_a$  and  $k_{lag}$  change with an initial concentration of  $Zn^{2+}$ . Value of  $k_a'$  shows closer to  $k_a$  at higher initial concentration of  $a$ . Changing values of  $k_a$  and  $k_{lag}$  indicates that  $k$  is not only affected by temperature, but also it considered a complex function of the initial sorbate concentration ( $a$ ). Intercept of Lagergren pseudo-first-order kinetics,  $\ln q_e$  always has a different value from the  $\ln q_e$  from experiments [38]. From eq. (8), it can be seen that the intercept plot  $\ln(q_e-q)$  vs.  $t$  is more complex functions. The results of the calculation of  $\ln((x_e(ab-x_e^2))/ab)$  of the data on  $a_1$ ,  $a_2$ , and  $a_3$  is -1.662; -1.637; -1.606, respectively. The calculations showed results nearly close to the value of

the intercept Lagergren kinetics equation in Table 2. Data of time variation of the concentration of the sorbate ( $a$ ) in this study indicates the proposed kinetics of the eq. (14) gives linearity which is similar to Lagergren kinetics equation and has value of intercept nearly close from calculation.

## CONCLUSION

HD-HA has physical apparent similar with PS-HA. Characterization HD-HA using spectrophotometer UV-Vis and FT-IR gives the characteristic pattern and characteristics absorption bands based on Stevenson (1994). The proposed kinetic expression derived from the second order sorption reaching equilibrium has been proved successfully to be applied to determine the value of intercept of the well known Lagergren equation which has same value with calculation of  $\ln((x_e(ab-x_e^2))/ab)$ . The proposed kinetics expression has the same condition with Lagergren kinetics model and gives better linearity at higher concentration of  $Zn^{2+}$ .

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