Research Article

Comparison the New Kinetics Equation of Non-competitive Sorption Cd(II) and Zn(II) onto Green Sorbent Horse Dung Humic Acid (HD-HA)

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Abstract

The new kinetics equation has been proposed and applied to the sorption of Cd(II) and Zn(II) onto green sorbent horse dung humic acid (HD-HA). This work aims to study the new kinetics equation and to compare its parameters with Lagergren and Ho kinetics equation in the same system. HD-HA was extracted and purified by Stevenson's methods and then characterized by detection of its functional group, UV-Vis spectra, and total acidity. The sorption study of this work was investigated by batch experiment in pH optimum 5. Langmuir's monolayer sorption capacity (b) of Cd(II) and Zn(II) onto HD-HA was 1.329×10^{-3} and 1.070×10^{-3} mole.g^{-1}, respectively. Langmuir equilibrium constant (K_L) of Cd(II) and Zn(II) sorption was 5,651 and 6,399 (mole/L)$^{-1}$, respectively. The kinetics parameters were determined by Lagergren, Ho, and the new kinetics equation. The best linearity (R^2) and the most fitted sorbed metal ion in equilibrium (x_e) with the experimental data was the Ho kinetics equation. However, the correct value of sorption rate constant (k_a) was not really known, because the k_a resulted from Ho and Lagergren kinetics equation can not be compared with another parameter and there is no scale to measure the correctness of this value of k_a. In this work, the correctness value of k_a of the new kinetics equation can be measured by k_a/k_d equal to K, and this K should be equal to K_L. The values of K of Cd(II) (3,452 (mole/L)$^{-1}$) and and Zn(II) (10,898 (mole/L)$^{-1}$) were quite similar with K_L. Additionally, the value of intercept from linear regression of this new kinetics equation (Cd(II) = 6.8517; Zn(II) = 6.0408) was highly similar with the manually calculation of $-ln(x_e/ab)$ (Cd(II) = 7.0638; Zn(II) = 6.9838). These new kinetics equations also reveal that Lagergren sorption rate constant (k_{Lag}) is the complex function of $k_a(ab-x_e^2)/x_e$. Copyright © 2018 BCREC Group. All rights reserved

1. Introduction

In the history of kinetics sorption, predicting the sorption rate of sorbate onto sorbed for a given system is probably the most important factor in sorption system design, with sorbate residence time and the reactor dimensions controlled by the system's kinetics [1]. A number of sorption processes for pollutants have been studied in order to find a suitable explanation for the mechanisms and kinetics for sorting out environment solutions. In order to investigate the mechanisms of sorption, various kinetic

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models have been suggested. In recent years, adsorption mechanisms involving kinetics-based models have been reported. The earliest study of kinetic sorption has been developed since past decade by Lagergren (1898) [2]. Lagergren presented a first-order rate equation to describe the kinetics of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal based on the sorption capacity [3]. It can be presented in Equation (1).

$$\frac{dx}{dt} = k_{lag}\left(x_e - x\right)$$ (1)

where x_e and x (mg.g-1) are the sorbate sorbed at equilibrium and at time t (min), respectively, and k_{lag} is the pseudo-first rate constant (min-1). Eq. (1) was integrated with the boundary conditions at $t = 0$ to $t = t$, and $x = 0$ to $x = x$, to yield linear form in Equation (2).

$$ln\left(x_e - x\right) = ln\left(x_e\right) - k_{lag}t$$ (2)

Taking regression between $ln(x_e\text{-}x)$ vs t on this equation generates straight line, where slope is $-k_{lag}$ and intercept is $ln(x_e)$. To distinguish the kinetic equations, based on sorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first order [3]. In recent years, it has been widely used to describe the adsorption of pollutants from wastewater in many different fields.

In 1995, Ho described the adsorption kinetics of divalent metal ions onto peat [4], in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as: aldehydes, ketones, acids, and phenolics, are responsible for the cation-exchange capacity of the peat. The main assumptions were that the adsorption may be second-order, and the rate limiting step, may be chemical adsorption, involving valent forces through sharing or the exchange of electrons between the peat and divalent metal ions. The rate expression of pseudo-second order equation is:

$$\frac{dq_t}{dt} = k_{Ho}\left(q_e - q_t\right)^2$$ (3)

where q_t and q_t (mg.g-1) are the sorbate sorbed at equilibrium and at time t (min), respectively. k_{Ho} (g.mg-1.min-1) is the pseudo-second rate constant. By integrating the equation with the boun-dary conditions at $t = t$ and $q_e = q_t$, it yields linear form as in Equation (4).

$$\frac{t}{q_t} = \frac{1}{k_{Ho}q_e^2} + \frac{1}{q_e}t$$ (4)

Regression between t/q_t vs t on this equation generates straight line, where q_e obtained from slope and k_{Ho} obtained from intercept.

Before the Ho kinetics equation, the other kinetics equations were proposed by Elovich [5-6], Ritchie [7], Sobkowsk and Czerwinski [8], and Blanchard *et al.* [9] equations. Elovich's equation was based on the adsorption capacity. This work was established though the work of Zeldowitsch by studying sorption of carbon monoxide on manganese dioxide. He found that sorbed gas was decreased exponentially with an increase in the amount of sorbed gas. It has commonly been called the Elovich equation in the following years. In 1977, Ritchie reported a model for the adsorption of gaseous systems. Assumptions were made as follows: θ is the fraction of surface sites which are occupied by an adsorbed gas, n the number of surface sites occupied by each molecule of the adsorbed gas, and a is the rate constant. In earlier years, Sobkowsk and Czerwinski presented a rate equation for the reaction of carbon dioxide adsorption onto a platinum electrode. They concluded that the first-order is only for low surface concentrations of a solid. In 1984, Blanchard *et al.* presented the overall exchange reaction of NH_4^+ ions fixed in zeolite by divalent metallic ions. In recent years, the Blanchard second-order expression has been used to describe the kinetics of exchange processes between sodium ions from zeolite A and cadmium, copper, and nickel ions from solutions [10]. The equation and the origin rate can be seen in Table 1.

In past two decade, the Lagergren and Ho kinetics equation dominate the sorption kinetics study in publication. These two kinetics sorption equation is the most used to describe kinetics and mechanism of sorption in any systems [1,11-12]. In many cases, there was weakness of using Lagergren and Ho kinetics equation because the parameters value of these kinetic equations seems to be independent and have not a clear explanation because it can not be compared with another parameter and there is no scale to measure the correctness of this parameters value. In other words, it can be stated that the kinetic parameter is unknown whether it is really correct or not. In Lagergren equation, the intercept value ($ln\ x_e$) from regression of plot $ln\ (x_e\text{-}x)$ vs. x is never be same with $ln\ x_e$ from manual calculation of experimental data [13]. The value of rate constant (k) was also changed with changing the initial concentration of sorbate [14]. Additionally, these both kinetics equation was not determined de-

sorption rate constant (k_d), where it was important in equilibrium system. This research proposed the new kinetics equation to give another view of kinetics sorption to overcome that weakness. The parameters obtained from this new kinetics equation can be compared with Langmuir data to confirm whether the parameters were really correct or not.

The new kinetics equation developed based on an approach that sorption is a dynamic equilibrium process and during mathematical derivation the availability of binding sites of sorbent of Langmuir model. The applicability of this new kinetic equation is then tested for the sorption of Cd(II) and Zn(II) on humic acid (HD-HA). These metal ion, Cd(II) and Zn(II) known as their distribution in soil and water has been to be strongly associated with the presence of humic substance [15]. HA was also reported to have widely used to reduce or eliminate metals in surface water [16-20]. HA generally extracted from peat soil as source. The usage of peat soil as source of HA has negative effect that is release stored carbon storage contributed to increasing the greenhouse effect [21]. Additionally, it can not be renewed immediately. To greening the source of HA, it can be used horse dung that it has high existence because it has a denser and rough texture, so it is rarely used for biogas and organic fertilizer [22]. The evaluation is carried out for the comparison the value of k_a of the sorption of Cd(II) and Zn(II) on HD-HA by Lagergren, Ho, and this new kinetics equation. The sorption kinetic model was also evaluated for intercept of Lagergren kinetics equation ($ln\ q_e$) often found not equal between $ln\ q_e$ from experiment [13] and the value of $k_a/k_d = K$ often was not same with Langmuir equilibrium constant (K_L). Furthermore, study of the new kinetics equation was also critically discussed in this paper.

2. Materials and Methods

2.1 Materials

All reagent used in this work are analytical grade, i.e. sodium hydroxide, hydrochloric acid, fluoride acid, silver nitrate, barium hydroxide, calcium acetate monohydrate, cadmium(II) acetate dihydrate, and zinc acetate dihydrate supplied by Merck Co. Inc. (Germany) and used without further purification. HD-HA was extracted from dry horse dung powder from Bantul, Yogyakarta. As standard of humic acid, PS-HA was extracted from peat soil from Musi Banyuasin, South Sumatra. Extraction and purification was performed according to the procedure of IHSS under atmospheric air [23].

2.2 Instrumentations

These work used Hanna Instrument Portable pH Meter, magnetic stirrer, glass ware, and

Table 1. The summary of historical kinetics equations

Author(s)	Ref.	Origin Rate	Linear form	Plot
Lagergren	[2,3]	$\dfrac{dx}{dt} = k_{lag}(x_e - x)$	$\ln(x_e - x) = \ln(x_e) - k_{lag}t$	*ln(x$_e$-x)* vs. *t*
Elovich	[5,6]	$\dfrac{dq}{dt} = ae^{-\alpha q}$	$q = \left(\dfrac{2.3}{\alpha}\right)\log(t+t_0) - \left(\dfrac{2.3}{\alpha}\right)\log t_0$ With $t_o = 1/a\alpha$	*q* vs. *log (t+t$_0$)*
Sobkowsk and Czerwinski	[8]	$\dfrac{d\theta}{dt} = k(1-\theta)^n$	$\dfrac{\theta}{1-\theta} = k_{SC}t$	*θ/(1-θ)* vs. *t*
Ritchie	[7]	$\dfrac{d\theta}{dt} = a(1-\theta)^n$	$\dfrac{q_\infty}{q_\infty - q} = \alpha t + 1$	*q$_\infty$/(q$_\infty$-q)* vs. *t*
Blanchard *et al.*	[9]	$-\dfrac{dn}{dt} = K(n_0 - n)^2$	$\dfrac{1}{n_0 - n} - \alpha = Kt$	*1/n$_0$-n* vs. *t*
Ho	[1,4]	$\dfrac{dq_t}{dt} = k_{Ho}(q_e - q_t)^2$	$\dfrac{t}{q_t} = \dfrac{1}{k_{Ho}q_e^2} + \dfrac{1}{q_e}t$	*t/q$_t$* vs. *t*

Jena ContrAA 300 Atomic Absorption Spectroscopy (AAS) to analyze total metal ions in sample. The characterizations of horse dung humic acid (HD-HA) and peat soil humic acid (PS-HA) were performed by Shimadzu FTIR Prestige 21 and UV-visible spectrophotometer (GBC Cintra 2020).

2.3 Extraction and Purification of HD-HA

The sorbent (HD-HA) and the standard (PS-HA) was extracted and purified by IHSS procedure [23] under atmospheric air. About 1 kg of sample (dry horse dung powder) was extracted based on acidity using 10 L NaOH 0.1 M, stirred for 24 hours, and the filtrate was taken by centrifugation at 3000 rpm. Filtrate was then added by 0.1 M HCl to reach pH 1, saved for 12 hours until two layers formed: humic acid (solid bottom layer). The crude HD-HA was separated by centrifugation at 5000 rpm for 15 minutes and dried at 60 °C. the same step conducted to extract PS-HA from dry peat soil powder. Crude HD-HA (and PS-HA) was purified by HCl/HF methods. About 50 g of crude sorbent was added into 0.1 M HCl / 0.3 M HF (1:1), stirred for 24, and the solid was taken by centrifuged at 5000 rpm. The Cl⁻ residues in the sample were removed by washing with distillate water and then the sample tested by silver nitrate to detect Cl⁻ residues. Purified sample, which was free of Cl⁻ ion, was then dried at 60 °C.

2.4 Characterization of HD-HA

Functional groups were determined by FT-IR performed by mixing the well ground of sample with spectroscopic grade pellet KBr and pressed into a disk. The spectrum of absorption band was analyzed in wavenumber ranges of 400 to 4000 cm⁻¹. Humification characterised by UV-Vis was performed by dissolving 10 mg of sample in pH 11 of 100 mL distilled water. Well mixed sample was inserted into a cuvet and analyzed at UV-vision region. Ash level analysis indicates the mineral content in sample. Ash level was determined by inserting 50 mg of sample into a crucible porcelain furnace at 750 °C for 4 hours. Each sample was repeated triplet and noted the changed of weight before and after furnace. Total of acidity was determined by Baryta indirect potentiometric titration method [23].

2.5 Effect of Medium Acidity

At first, a series of 50 mL of Cd(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 Cd(II) solution, 10 mg of HD-HA was poured and then stirred for 2 h. After filtering through 100 mesh membrane filter, the concentration of Cd(II) in supernatant was analyzed by using AAS. Sample and blank solutions were analyzed under same conditions. The amount of sorbed Cd(II) was considered to be the difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed. The same procedure was conducted to pH optimum Zn(II).

2.6 Sorption Isotherm

The sorption isotherm experiments were carried out using a batch type reactor using 50 mL of Erlenmeyer in a water bath at 25±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 Cd(II) at pH 5.0 for 2 h and then aged for 24 h. After separating the supernatants, the concentration Cd(II) in the supernatant was determined by AAS. Under the same condition with the sample solution, the blank solution was also analyzed. The same procedure was performed to the Zn(II) sample. The data obtained was then analyzed by Freundlich and Langmuir isotherm models.

2.7 Sorption Kinetics

The kinetics experiments also were carried out using a batch type reactor using 50 mL Erlenmeyer in a water bath at 25±0.01 °C. The volume of sorption medium was 50 mL, the initial metal ion concentration was 50 mg/L, the acidity was adjusted at pH optimum; and to each solutions, 10 mg of sorbent was added and then stirred continuously at 10, 15, 20, 25, 30, 35, 40, 45, 60, 90, and 120 minutes. The sample was immediately filtered through 100 mesh filter and the concentration of Cd(II) in the supernatant was analyzed by using AAS method. Sample and blank solutions were analyzed under the same conditions. The amount of sorbed Cd(II) was considered to be difference between the initial and the remaining amount in the reacting solution each time a sample was analyzed. The same procedure was performed to Zn(II) and data obtained was then analyzed by three different sorption kinetics models, i.e. new kinetics equation, Lagergren equation, and Ho equation.

3. Results and Discussion

3.1 Characterization of HD-HA

The dark brown powder of sorbent (HD-HA) has the texture and appearance highly similar to peat soil humic acid (PS-HA). Characterization by UV-Vis spectrophotometer of HA is smoothly decreased and there are no maximum or minimum clear peak with increasing wavelength (Figure 1). The high absorbance emerges in the UV region and then decrease smoothly to visible region.

The smooth patterns from this study were similar to Stevenson's [23] and Agarwal's *et al.* [24] study. Characteristic of amount aromatic compounds (C=C, C=O, and C=N) and degree of humification were indicated in range of 250–300 nm. High absorbance of UV spectra of humic substance was commonly used to predict several molecular properties of humic substance. Prominent region should be spot approximately at 280 nm (A_2), 400-500 nm (A_4), and around 600 nm (A_6). The combination ratios of this absorbance indicates specific character of humic substances. $A_{2/4}$ indicates the portion of lignin and other materials at the beginning of the humification process [25]), while $A_{2/6}$ indicates the portion between humificated and nonhumificated material. $A_{4/6}$ indicates degree of condensation and polymerization of aromatic compounds (can be used to predict humification index) (Table 1). This combination ratio of UV-Vis spectra of HD-HA and PS-HA can be used to predict the humification index (maturity) that any correlation to content of acidity and sorption capacity. The lower value of $A_{2/6}$ and $A_{4/6}$ represents a higher degree of aromatic and maturity of organic material. The ratio $A_{4/6}$ for HA should be lower than 5, while FA is ranged 6 to 8.5 [23]. $A_{4/6}$ ratio of PS-HA was higher than 5 (6.25) indicating the peat soil from Musi Banyuasin still young and humification still occur. The $A_{4/6}$ ratio of HD-HA was also higher than standard and PS-HA. It is indicated that horse dung used in this work has not been humificated well.

Success purification makes clear the clay minerals, silicates, and disturbing metal impurities from sorbent [23], which is cover the surface of HD-HA. This impurities interact with active site of HD-HA, -COOH and phenolic –OH which affected the total acidity and the –COOH and phenolic –O content. The lower ash level indicates that material have low of impurities. The yield of ash level of sorbent before purification were above 5 % (w/w), however after purification process, the results of ash level of PS-HA and HD-HA decrease below 5 % i.e. 0.99 and 1.20 (% w/w), respectively. Total acidity of HD-HA was also increased after purification process, but it is still below the total acidity of PS-HA and reference HA [23]. The lower total acidity agrees with fact that horse dung material used in this study is taken from open area and only about 3 month ages (Table 2). This result indicates the successfulness of purification process.

Comparison the FT-IR spectra of crude HD-HA, purified HD-HA, crude PS-HA and purified PS-HA showed that both of HD-HA and PS-HA have high similarities in particular wave number absorption band of the functional group (Figure 1). There are five characteristic band of HA according to HA reference [23], i.e. 3300-3600 cm^{-1} indicates O–H bond with hydrogen bond occurs inter molecule of active site
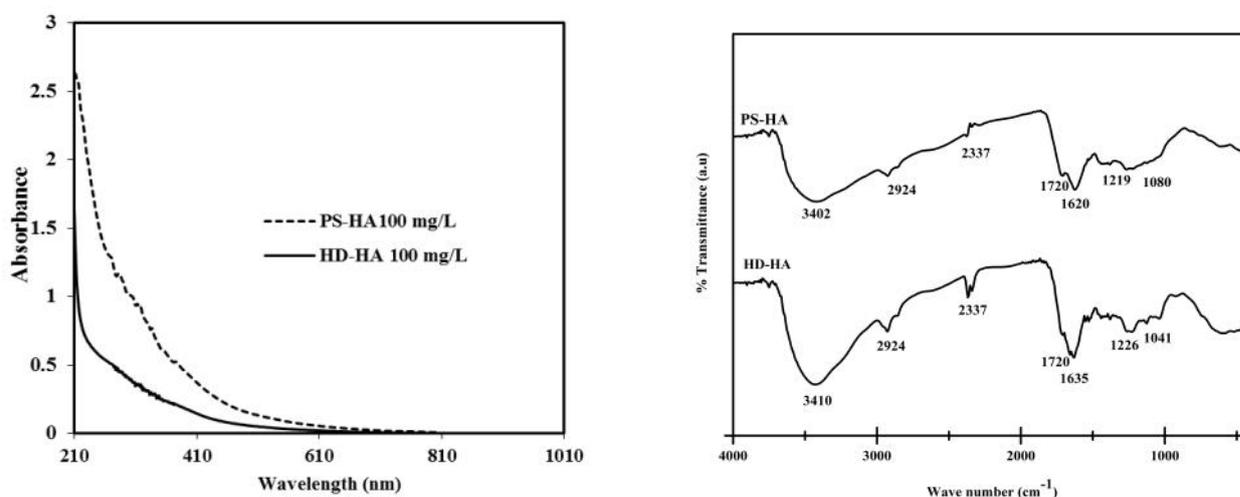

Figure 1. The characteristic pattern of UV-Vis absorbance (left) and FT-IR spectra of HD-HA and PS-HA (right)

HA that makes the band wider, about 2900 cm^{-1} indicates C–H aliphatic stretching, about 1720 cm^{-1} indicates carbonyl group of –COOH, about 1600 cm^{-1} indicates phi of aromatic alkene and aromatic rings of quinones which form hydrogen bond with –OH group, and about 1200 cm^{-1} indicates stretching of C–O from –COOH group. Additional sharp peak commonly emerged at 2330 cm^{-1} which is not come from HA, but come from C=O stretching of carbon dioxide trapped in KBr pellet. Similar band as a characteristic of HA was also reported by Barot and Bagla in study of extraction HA from dry cow dung powder [26,28].
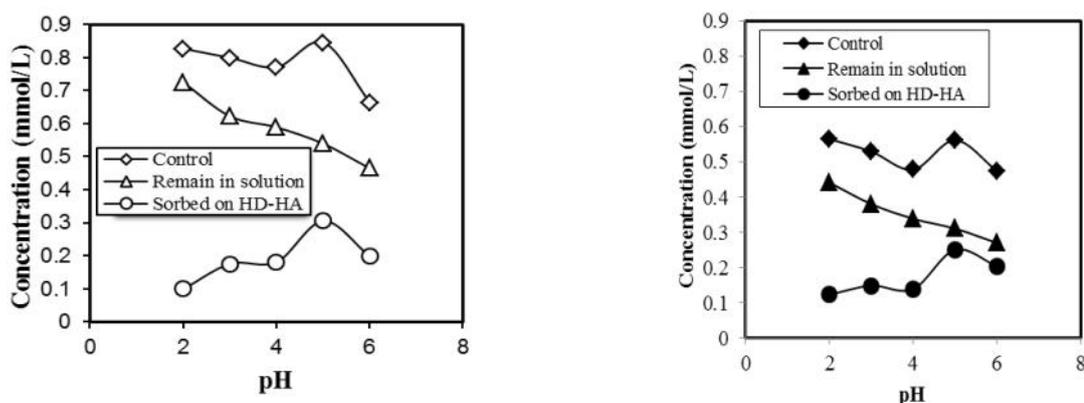
3.2 Effect of Medium Acidity

Acidity is a function of amount H^{+} in solution medium. It has high effect on the form of chemical substance or metal substance in aqueous medium [27]. Lower pH (high acidity) affects in decreasing the metal ions that attached in active site of sorbent as a result of competition between H^{+} which the consequences is high concentration of unsorbed metal ions in solution. The result off this work indicates that the concentration of both sorbed Cd(II) and Zn(II) tend to increases with the decreasing of medium acidity (Figure 2). At higher pH medium, amount of hydronium (H^{+}) ion was protonated and led to strong interaction among hydrogen and functional group of intermolecular HD-HA. In other word, the active site of HD-HA was detected in –COOH or –OH form which cause the surface has positively charged and leads to repulsion between metal ions and functional group of HD-HA. Caused by this repulsion, the metal ions (Cd and Zn) which sorbed in HD-HA was very low. This condition makes attached metal ions on sorbent very low. There is no significant differences between sorbed Cd(II) and Zn(II), although the Zn(II) seems little higher sorbed than the Cd(II). This result can be compared to previous study that the Zn(II) was sorbed higher than Cd(II). When the pH of medium acidity higher than 2, HD-HA's active site, -COOH and phenolic –OH start to be deprotonated that led to weakening in hydrogen bonds and the surface cover with negative charge. As a result, metal ion, Cd(II), and Zn(II) are easier to interact with active site of HD-HA and makes metal ion highly sorbed

Table 2. The absorbance ratio of UV-Vis spectra, ash level, and total acidity of HD-HA compared to PS-HA and Humic Acid reference

| Materials	Absorbance Ratio			Ash Level (% w/w)	Total Acidity (mol.kg^{-1})
	A_{280}/A_{472} ($A_{2/4}$)	A_{280}/A_{664} ($A_{2/6}$)	A_{472}/A_{664} ($A_{4/6}$)		
HD-HA	41.94	6.28	6.68	1.20	415.30
PS-HA	34.99	5.60	6.25	0.99	565.00
Humic Acid [14]	-	-	3.0-5.0	-	560.00-890.00
Fulvic Acid [14]	-	-	6.0-8.5	-	640.00-1420.00

Figure 2. Effect of medium acidity on the distribution of Zn(II) (left) and Cd(II) (right) in the presence of HD-HA

on sorbent. This condition is good for metal ion, but it is poor for HD-HA because it begins to dissolved and to form liquid phase, and it is hard to be separated. Optimum pH was balance condition between metal ions and HD-HA (sorbent) condition. The optimum pH of sorption Zn(II) and Cd(II) was occurred in pH 5. The optimum pH 5 was also suggested by Rahmawati and Santosa [18] and Burhan [28].

3.3 Sorption Isotherm

Determination of capacity and sorption energy of metal ions on HD-HA was plotted using Langmuir and Freundlich isotherm models. Langmuir isotherm model was derived from model described as follow:

$$A \quad + \quad S \quad \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \quad A*S$$
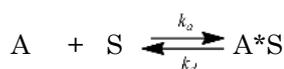
At time = 0 : $a=C_o$ b -
Sorbed   : m m m
In equilibrium: $a\text{-}m=C_e$ $b\text{-}m$ m

where $a = C_o$ is initial concentration of metal ion A (mole/L); b is sorption capacity (mol/g); m is amount metal ion A sorbed per gram sorbent, S in equilibrium (mole/g); and $a\text{-}m=C_e$ is concentration metal ion A in equilibrium (mole/L). From that model, equilibrium constant, $K,$ can be written in Equation (5).

$$K = \frac{[A*S]}{[A][S]} = \frac{m}{(b-m)C_e} \qquad (5)$$

Equation (5) can be rearranging:

$$m = \frac{KC_e b}{1 + KC_e} \qquad (6)$$

Linear form of Equation (6) was well-known called as Langmuir isotherm [29] model that can be written as:

$$\frac{C_e}{m} = \frac{1}{Kb} + \frac{1}{b}C_e \qquad (7)$$

Freundlich isotherm [30] form is $m = K_F C_e^n$. This model can be writing as linear form:

$$log\,m = log\,K_F + \frac{1}{n}log\,C_e \qquad (8)$$

where C_e is the equilibrium concentration in solution; b is Langmuir's sorption capacity; K represents Langmuir's constant of equilibrium; m is metal sorbed per gram sorbent at equilibrium; B is Freundlich's sorption capacity and, n is constants.

The application of the two models was resulted the sorption parameters shown in Figure 3. 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. Sorption capacity of Cd(II) and Zn(II) was 1.070×10^{-3} and 1.329×10^{-3} mole/g, respectively. Compared with Cd(II), Zn(II) have higher sorption capacity (Table 3). Sorption capacity of Cd(II) on HD-HA is less compared with another HA from other source as studied by Rahmawati and Santosa (HA from Rawa Pening peat soil, $b = 3.83 \times 10^{-3}$ mole/g) [18] and higher than Burhan (HA from dry cow dung powder, $b = 8.85 \times 10^{-4}$ mole/g) [28]. This can be explained by two reason, firstly atomic radii for Cd(II) actually higher than Zn(II) (1.4 Å and 1.1 Å, respectively), but in hydrate conditions Zn(II) has higher radii than Cd(II) (6 Å and 5 Å, respectively).

One of the sorbed mechanism metal ions onto functional group in HD-HA is water bridge [27]. This mechanism can be proved from ratio monolayer sorption capacity of Cd(II) and Zn(II) closely match with ratio hydrate radii for Cd(II) and Zn(II), that was 5 : 6. Secondly, Zn(II) has stronger acid characteristic than Cd(II), so that Zn(II) was more suitable with functional group of HD-HA which has more hard base characteristic. It is proved from comparison between Langmuir monolayer sorption capacity and Freundlich multilayer sorption capacity for Cd(II) is 19.9 times greater and Zn(II) is 64.6 times greater. Additionally, Zn(II) has greater sorption energy than Cd(II) (Table 4).

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 [27]. FT-IR studies showed that -COO- plays an important role in metal complexation. 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. Because metal ions occupy the active site, the strongest interaction occupies first and then the active side with lower energy. Meanwhile, the capacity (multilayer or multi-energy) indicates the Freundlich adsorp-
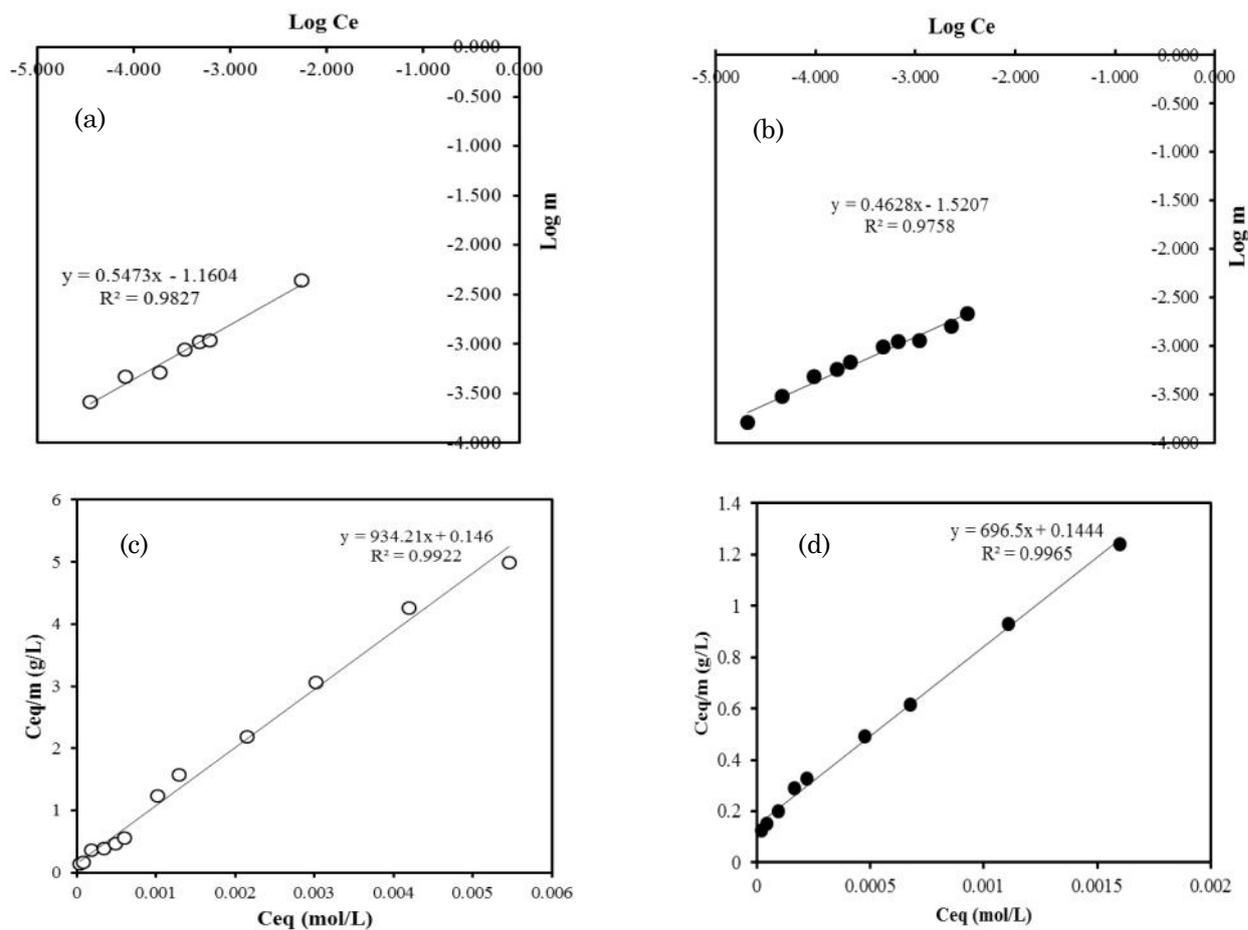
Figure 3. Freundlich isotherm sorption of Zn(II) (a) and Cd(II) (c) onto HD-HA and Langmuir isotherm sorption of Zn(II) (b) and Cd(II) (d) onto HD-HA

Table 3. Functional group content and total acidity of varied HA

Materials	Total Acidity (cmol/kg)	Carboxylate (cmol/kg)	-OH phenolic (cmol/kg)
HD-HA (This Work)	415,3	166,3	249,0
PS-HA (This Work)	565,0	208,2	356,8
Cow Dung-HA [20]	96,7	7,3	89,4
PS-HA [7]	715,8	326,6	426,2
PS-HA [14]	560,0 - 890,0	150,0 – 570,0	20,0 – 490,0

Table 4. 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 Cd(II) onto HD-HA

Metal ions	Sorption parameters						
	Langmuir				Freundlich		
	b (10^{-3} mol/g)	K (mol/L)$^{-1}$	E^{a} (kJ/mol)	R^2	B (10^{-2} mol/g)	n	R^2
Cd(II)	1.329	5,651	21.55	0.997	2.646	2.218	0.976
Zn(II)	1.070	6,399	21.86	0.992	6.912	1.827	0.983

[a]E= -RT ln K

tion capacity -COO- and all active side together. Interactions were occurred allegedly as electrostatic forces between the metal ions with active sites of HD-HA. FT-IR spectra can provide little information about the electrostatic interaction between sorbate and sorbent (Figure 4). The weakening of the C=O absorption of -COOH on wave number 1720 cm^{-1} after interaction with Cd(II) indicates the physical interaction of C=O group on the HD-HA acid with Cd(II).

3.4 The New Kinetics Equation

Considering the sorption of metal ions on sorbent is an equilibrium process as illustrated as follow:

$$A \; + \; S \; \underset{kd}{\overset{ka}{\rightleftharpoons}} \; A*S$$

At time, t= 0 a b -
At time, t = t a-x b-x x

where A is a metal ions; S is an sorbent (HD-HA); k_a is the sorption rate constant, and k_d is 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), from the same derivation as Langmuir, the equation rate can be written in Equation (9).

$$r_{ads} = \frac{dx}{dt} = k_a (a-x)(b-x) - k_d x \qquad (9)$$

At equilibrium, dx/dt=0, so that:
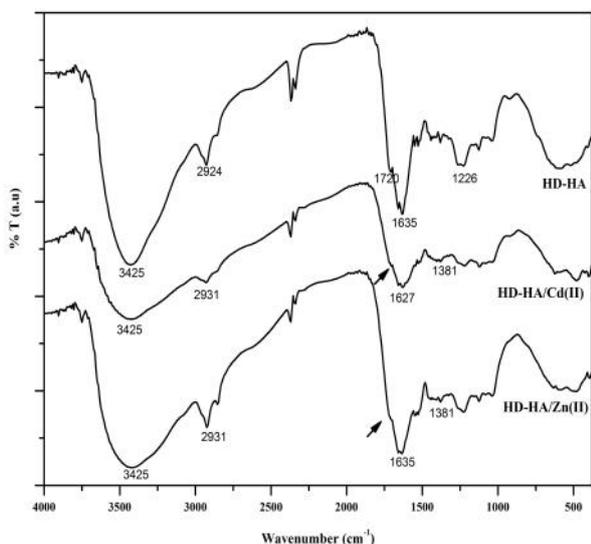
Figure 4. FT-IR spectra of HD-HA before and after interaction with metal ions, Cd(II) and Zn(II)

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

Substituting Eq. (9) into Eq. (10) yields:

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

It can be simplify be a simple form:

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

At $t = 0$, sorption has not occured yet, so k_a is 0 and metal ion of A has not been adsorbed on sorbent S, so $x = 0$. Taking integration for the eq. (12) with limit (ab) to (ab-$x_e x$), 0 to (x), and 0 to t, so Eq. (12) can be written as:

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

$$(13)$$

Integration results:

$$ln\left(\frac{(ab - x_e x)x_e}{(x_e - x)ab}\right) = k_a \frac{ab - x_e^2}{x_e} t \qquad (14)$$

Rearranged Eq. (14) gives:

$$ln\left(\frac{ab - x_e x}{x_e - x}\right) = k_a\left(\frac{ab - x_e^2}{x_e}\right)t - ln\left(\frac{x_e}{ab}\right) \qquad (15)$$

Or in another form:

$$ln(x_e - x) = ln\left(\frac{x_e(ab - x_e x)}{ab}\right) - k_a\left(\frac{ab - x_e^2}{x_e}\right)t \qquad (16)$$

The Eq. (16) is surprisingly the same as Lagergren equation, $ln\,(q_e$-$q_t) = ln(q_e) - k_{lag}\,t$, where q_e and x_e has the same unit (mole/L). Thus allegedly linearity of Eq. (16) is similar to the linearity Lagergren pseudo-first order. The same plot between Eq. (16) with a Lagergren pseudo-first-order model is $ln\,(x_e$-$x)$ versus t generates relationships, $k_{lag} = k_a\,((ab$-$x_e^2)/x_e)$. If the Eq. (16) gives 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 Aharoni and Sparks [13] why the parameter $ln\,q_e$ always have different values with $ln\,q_e$ obtained from experimental data.

3.5 Sorption Kinetics

If Eq. (15) is applied, plot $ln\,((ab$-$x_e x)/(x_e$-$x))$ vs t generates straight line and the value of k_a can be determine from slope. Intercept was $-ln\,(x_e/ab)$ and should not be different with

from calculation $-ln \ (x_e/ab)$ from experimental data. The value of k_d can be determined from Eq. (10), and if we divide k_a with k_d yields equilibrium constant, K, in which the value of K should not be different from K of isotherm Langmuir. Kinetics profile of sorbed metal ions as function of time can be seen in Figure 5.

This experiment used 10 mg sorbent and 50 mL of Cd(II) and Zn(II) 50 mg/L, so initial concentration of Cd(II), a_{Cd} = 4.355×10^{-4} mol/L (Ar Cd = 112.4) and initial concentration of Zn, a_{Zn} = 8.075×10^{-4} mole/L (Ar Zn = 65.4). Sorption equilibrium reach after 120 minute interaction, yielded sorption Cd(II), $x_{e(Cd)}$ and Zn(II), $x_{e(Zn)}$ at equilibrium was 1.353×10^{-4} mole/L and 1.865×10^{-4} mole/L, respectively. Sorption capacity, b of Zn(II) and Cd(II) from Langmuir isotherm, is 1.070×10^{-3} and 1.329×10^{-3} mole/g, respectively. If we assume b is a species, it interacts with metal ions A in certain volume, so we can change b into mole/L unit as a, so b = 2.657×10^{-4} mole/L. Plot data into three kinetics expression, i.e. Lagergren pseudo-first order [2], Ho pseudo-second order [1], and this new kinetics equation [14], can be seen in Table 5.

In many publications about kinetics equation study, linearity (R^2) of linear regression is one of the most suitable parameter of any kinetics equation [31-34]. In this work, the best linearity was Ho kinetics equation (R^2 in Cd(II) sorption = 0.995; Zn(II) = 0.999). The most fitted calculation of x_e with experimental value of x_e was also achieved by Ho kinetics equation. The closeness of experimental value of x_e of

Cd(II) and Zn(II) was 1.353 and 1.865 mole/L, respectively, and calculation value of Ho kinetics equation of Cd(II) and Zn(II) was 1.531 and 1.897 mole/L, respectively, as seen in Table 5. The best linearity (R^2) and the most fitted x_e between experiment and calculation confirmed by Sheela *et al.* [31]. The Ho kinetics equation was also the most fitted linear regression in the most adsorption system [31-34]. However, explanation about the kinetics equation itself is rarely discussed. One of them, sorption rate constant (k_a) was resulted from Ho and Lagergren kinetics equation. These both value of k_a, after equated the unit, was always different. This value of k_a was independent and can not
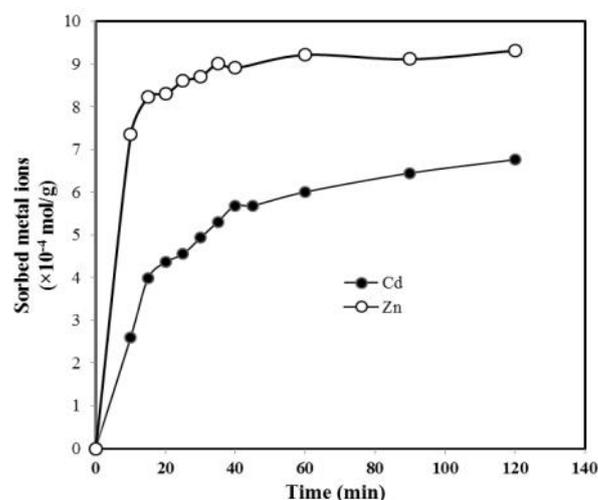

Figure 5. Sorption profile of Cd(II) and Zn(II) on HD-HA as a function of interaction time

Table 5. The comparison of linearity and kinetics sorption parameters of 50 mL metal ions 50 mg/L onto 10 mg HD-HA in pH 5 at 0-120 minute

Metal ions	Experiment	Pseudo-first order (Lagergren)			Pseudo-second order (Ho)			New kinetics equation		
	x_e (mol/L) × 10^{-4}	R^2	k_{lag} (min^{-1}) × 10^{-2}	x_e (mol/L) × 10^{-5}	R^2	k_{Ho} (min^{-1} (mol/L)$^{-1}$) × 10^3	x_e (mol/L) × 10^{-4}	R^2	k_a (min^{-1} (mol/L)$^{-1}$)	k_d (min^{-1}) × 10^{-2}	x_e (mol/L) × 10^{-4}
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Cd(II)	1.353	0.976	3.07	9.137	0.995	5.217	1.531	0.982	43.178	1.250	1.094
Zn(II)	1.865	0.961	5.62	6.00	0.999	2.179	1.897	0.980	73.215	6.718	0.726

Table 6. Comparison parameters between manually calculation and linear regression of new kinetics equation

Metal ions	$-ln \ (x_e/ab)$ of new kinetics equation		$k_a/k_d=K$		Intercept of plot $ln \ (x_e-x)$ vs t		k_{lag} and k_a	
	Calculation	Intercept from regression	$k_a/k_d=K$ from regression (mol/L)$^{-1}$	K from Langmuir eq. (mol/L)$^{-1}$	$ln \ q_e$ of Lagergren equation	Calculation $ln(x_e(ab-x_e^2))/ab)$	k_{lag} from Lagergren eq. (min^{-1})	k_{lag} from $k_{lag}=k_a$ $(ab-x_e^2)/x_e)$ (min^{-1})
Cd(II)	7.0638	6.8517	3,452	5,651	-9.3005	-9.0807	0.0307	0.0311
Zn(II)	6.9838	6.0408	10,898	6,399	-9.7206	-6.984	0.0561	0.0562

be compared with another parameter. There is no scale to say that the parameter (k_a) was really correct. The correlation parameters for the Lagergren and Ho kinetics equation were low and the calculated x_e values obtained from the Lagergren kinetic equations are not reasonable values [32]. In this work, beside the parameters of new kinetics equations has good correlation to Langmuir data, the parameters can also be compared among calculation and experimental data (Table 6).

Application of Eq. (15) as the new kinetics equation on sorption data of Cd(II) and Zn(II) onto HD-HA results good linearity between $ln \ ((ab\text{-}x_ex)/(x_e\text{-}x))$ vs t, which R^2 higher than Lagergren pseudo-first order expression (Figure 6). Best linearity obtained by Ho pseudo-second order expression which $R^2 = 0.999$ for Zn(II) and 0.995 for Cd(II). This evidence proves that Ho kinetics expression has suitable condition of experiment comparison between initial concentration of metal ions (a) and sorption capacity (b) which is approximately 2:3 for Cd(II) and 1:4 for Zn(II). However, both Ho and Lagergren have not good relationship with data from Langmuir sorption isotherm. Sorption rate constant, k_a, resulted from slope in Eq. (15), was 73.215 (min^{-1} (mole/L)$^{-1}$) for Zn(II) and 43.18 (min^{-1} (mole/L)$^{-1}$) for Cd(II). Meanwhile, desorption rate constant, k_d, resulted from Eq. (10) was 6.718×10^{-3} min^{-1} for Zn(II) and 1.250×10^{-2} min^{-1} for Cd(II). If we divide k_a with k_d from this new kinetics equation yields equilibrium constant, K, which was 3,452 (mole/L)$^{-1}$ for Cd(II) and 10,898 (mole/L)$^{-1}$ for Zn(II). From Langmuir data, it was observed that sorption equilibrium constant, K_L Cd(II) and Zn(II) was 5,651 and 6,399 (mole/L)$^{-1}$), respectively. The comparison value between K from new kinetics equation and K_L from Langmuir data shows that sorption Cd(II) has closer value (3,452 (mole/L)$^{-1}$ to 5,651 (mole/L)$^{-1}$) than sorption Zn(II) (10,898 (mole/L)$^{-1}$ to 6,399 (mole/L)$^{-1}$). This evidence proves that the parameter of new kinetic equation can be confirmed with Langmuir isotherm data.

The value of equilibrium constant in both K from new kinetics equation and K_L from Langmuir isotherm should be equal. From our previous work, the differences of this value K and K_L generates from ratio of initial concentration of sorbate (a) and sorption capacity (b) [14]. Because the k_a, k_d, and x_e are the function of a and b [14]. It might be the correct that ratio of a and b generates the equal K and K_L. Additionally, every sorbent and sorbate has the own this ration for equality of K and K_L.

The values of k_a, k_d, and x_e from new kinetics equation can be seen in Table 4. The value of k_a, k_d, K, and E of Zn(II) was higher than k_a, k_d, K, and E of Cd(II). The higher value of k_a, k_d, and K was caused by suitability hard-hard characteristic between Zn(II) and functional group of HD-HA. The higher value of k_a and k_d means that Zn(II) sorbed faster than Cd(II), but Zn(II) also desorbed greater then Cd(II). It was proved that in 60th minutes, Zn(II) has reached the equilibrium, but Cd(II) sorption still increases till more 120th minute (Figure 5). The suitability of hard-hard characteristic between Zn(II) and functional group of HD-HA lead the faster sorption, but the bigger hydrate radii of Zn(II) (6 Å) than Cd(II) (5 Å) cause the sorption capacity of Cd(II) higher than Zn(II) (Table 4). Smaller hydrate radii of Cd(II) than Zn(II) leads to higher amount of sorbed Cd(II).

Aharoni and Sparks [13] stated that intercept from Lagergren linear regression, $ln \ q_e$ always have different values with calculated $ln \ q_e$ obtained from experimental data. In the same unit (mole L^{-1}) of eq. (16) and Lagergren kinetics equation we can conclude that $ln \ q_e$ of Lagergen kinetics equation is a more complex function of initial metal ion concentration (a), sorption capacity (b), and sorbed metal ion at equilibrium (x_e). The evidence of this statement was calculation of $ln \ (x_e(ab\text{-}x_e^2)/ab)$ give nearly close value with $ln \ q_e$ from Lagergren equation (Table 6). Eq. (16) proves that k_{lag} was a complex function from $k_a \ ((ab\text{-}x_e^2)/x_e)$. This result answered question by Aharoni and Spark [13], that intercept should have similar value between calculation and regression. These results proves that the new kinetics equation has more advantages in determining sorption rate constant, k_a, desorption rate constant, k_d, and equilibrium constant, K, from single set data comparing both Lagergren and Ho kinetics expression. This new kinetics equation also has good relation between parameters resulted from manually calculation and linear regression, which was not owned by other kinetics equation.

4. Conclusions

It was obviously observed from physical appearance, total acidity, UV-Vis, and FT-IR study that horse dung can be source of humic acid. It was proved that this new kinetics equation have good relation between parameters resulted from manually calculation and linear regression, which is not seen on other sorption kinetics equation. The new kinetics equation

was successfully applied to determine the value of intercept of the well-known Lagergren equation which has nearly close value with calculation of $ln\ ((x_e(ab-x_e^2))/ab)$, the value of equilibrium constant, $K = k_a/k_d$ from proposed kinetics expression which fairly close with equilibrium constant from Langmuir isotherm model (K_L), and intercept of this new kinetics equation $(-ln\ (x_e/ab))$ was nearly close with $-ln\ (x_e/ab)$ from the calculation. Additionally, this new kinetics equation has more advantages in deter-mining sorption parameters, i.e. k_a, k_d, and K from single set data comparing both Lagergren and Ho kinetics expression.
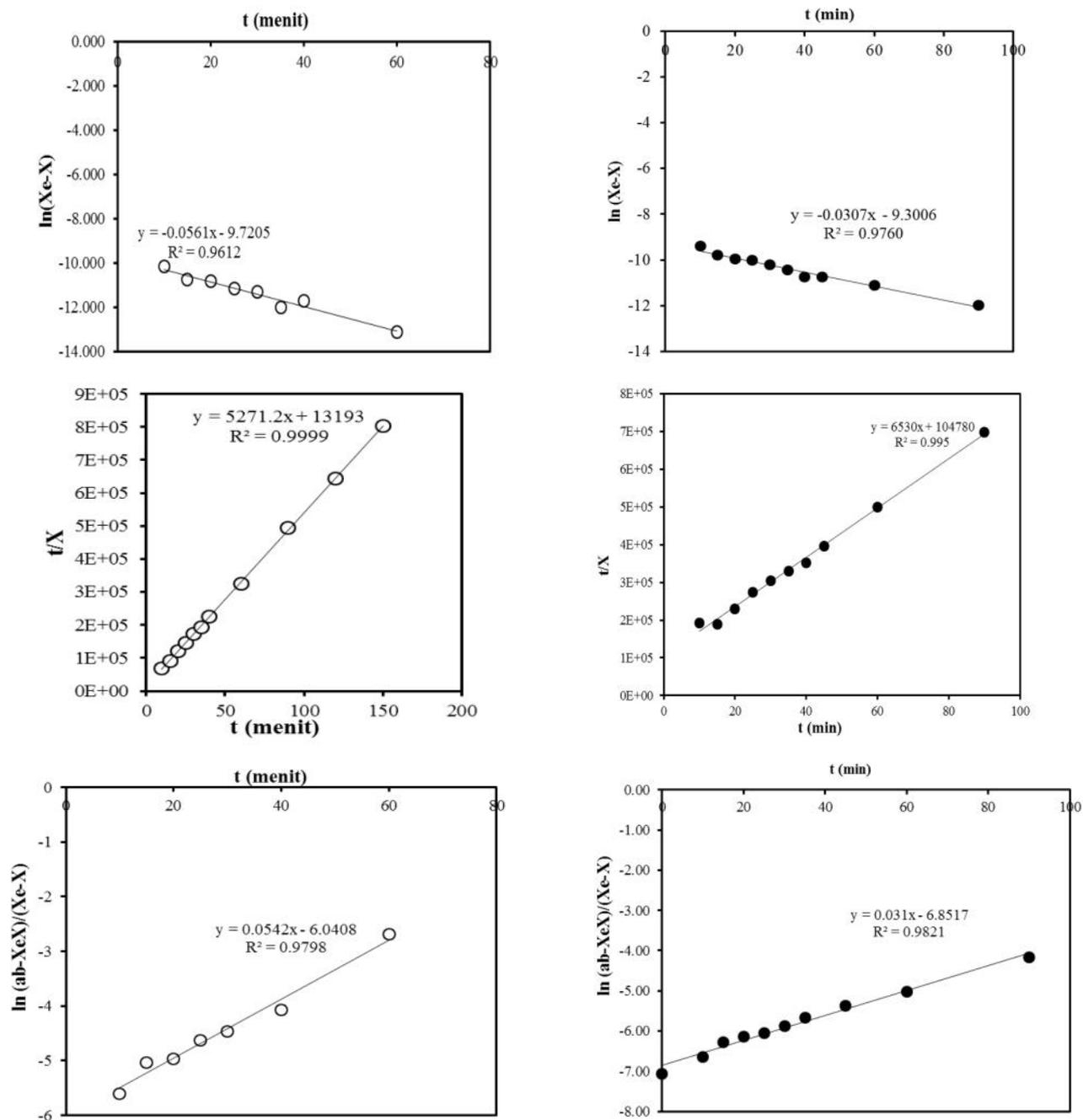
Figure 6. Linearity from regression of pseudo-first order Lagergren, pseudo-second Ho, and the kinetics equation of Zn(II) (left-from above to down, respectively) and Cd(II) (right-from above to down, respectively) onto HD-HA

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