ISOTHERMS AND CAPACITY ADSORPTION OF Fe(III) ONTO DUCK FEATHER MODIFICATION USING CH₃OH AND HCl SOLUTION

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ABSTRACT
Research has been carried out on isotherms and adsorption capacity of Fe (III) by duck feathers modification using CH₃OH and HCl solution. Activated duck feather adsorbents 2 g of duck powder was dissolved in 25 mL HCl with a concentration of 2; 4; 6; 8; and 10% (v/v), and 50 mL CH₃OH 25% was added, then placed on hotplate stirrer at 50 °C and stirred for 24 hours. The results showed that adsorption capacity of Fe by adsorbent of duck feather optimum before & after activation with 4% HCl - CH₃OH 25% were 111.11 mg/g and 125.00 mg/g and the kinetics follows Langmuir and Freundlich isotherms.

Keywords: Adsorption, Fe(III), Isotherm, Duck Feather

INTRODUCTION
The increase of duck breeding efforts can lead to an increased produce duck feather waste. Based on data from the Livestock Service Office of South Kalimantan Province in 2017, the number of ducks is 4,284,284 population, are generated can be estimated that a total of 200 tons of duck feather waste. These duck feathers to be used as adsorbents for absorbing metals and dyes in industrial wastewater. Related studies absorbent with formic acid, to Methylene Blue, the adsorption capacity of 134.76 mg/g¹ chicken feather adsorbents as removal of Indigo Carmine dyes², and Blue AstraZon 2RN textile dye (DBA).³ Modified chicken feathers with acylates for film and tested on textile waste.⁴ Research on chicken feathers as a metal absorber has been done with activation of Na₂S capable of absorbing Pb of 98.69%, duck feather composite with NaOH increased adsorption capacity on Cu²⁺ and Cr⁶⁺.⁵ The Co(II) adsorption study by the protein grains produced from chicken feathers suggests that it is more efficient.⁶ Research on adsorption of copper with Dromaius novaehollandiae feathers and chitosan composite that maximum adsorption was found 93.91% (18.78 mg/l), and these composites can be applied for safe, effective and economical industrial wastewater treatment, with a value of permitted threshold of 1.3 mg / L for drinking water.⁷ Lead adsorption (Pb) by duck feather adsorption capacity was 2.3 g / L⁸ on research of Pb²⁺, Cd²⁺ and Ni²⁺ by CH₃COOH modified chicken feathers and HCl showed that significant effect on adsorption of Pb²⁺, for the desorption process affected Pb²⁺ and Cd²⁺, but no significant effect on Ni²⁺.⁹ Adsorption As (III) modified chicken feathers by NaOH, Na₂SO₃, and CH₃OH showed that keratin from 6% CH₃OH and 2% HCl, CH₃OH higher when compared with the addition of NaOH and Na₂SO₃, adsorption capacity 0.13 mg/g.¹⁰ Research kinetics and equilibrium of metal adsorption have been carried out, among others. Adsorption almond shell activated carbon follow the Langmuir isotherms and adsorption capacity 334.40 mg/g.¹¹ The Langmuir and Freundlich isotherms are Cd by modification of chicken feathers with ascorbic acid¹², Cu, Zn and Ni by chicken feathers.¹³ Zn using powdered cow hooves¹⁴, Selenium (Se) using rice husk ash (RHA)¹⁵, Ni, Cu and Co on barley straw ash¹⁶, remove Ni and Cr from waste¹⁷, biosorption metal and Cu.

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by rice husk ash (RHA)\textsuperscript{18-19}, by active teff straw (ATS)\textsuperscript{15}, that Pb<Cd<Zn<Cu with an adsorption capacity 172 mg/g adsorbent.\textsuperscript{20} From the explanation above, it becomes important to research the modification of the feather keratin ducks using HCl and CH\textsubscript{3}OH at higher concentration variations to increase the capacity of adsorption especially for ion Fe, as well as study isotherms.

**EXPERIMENTAL**

**Preparation Duck Feather Powder**

Samples of duck feathers were from Banjarbaru, South Kalimantan, Indonesia. One kg of duck feather is washed with water and detergent, then dried in the sun and the smell is gone, heated by the oven for 24 hours at a temperature of at 50\(^\circ\)C, until all the water comes out. The duck feather is milled using a feather grinder and sieved using a 40 mesh sieve. 20 grams of duck feather powder soaked with 300 ml of 0.1 M HCl and 300 ml of petroleum ether for 24 hours, then washed with aqua dest, and filtered using a Buchner filter. The obtained residue is dried with an oven at 60\(^\circ\)C. Duck feathers to be used are washed first with water and detergent to remove the smell and dirt attached. Drying is done in sunlight aims to remove water content after the washing process, then proceed to dry using an oven to remove the remaining water content. The duck feathers are then milled using a feather grinder machine and sieved with a size of 40 mesh to enlarge the surface area of duck feathers. Fine duck powder is soaked with 0.1 M HCl to remove impurities or other minerals (demineralization). The duck feather filtered, then soaked with petroleum ether to remove fat. Samples were analyzed by Fourier Transform Infrared (FTIR 8201PC Shimadzu, Japan)

All experiments were at room temperature (30-31\(^\circ\)C). Activated of duck feather adsorbents that 2 g of duck powder was dissolved in 25 mL HCl with a concentration of 2\%; 4\%; 6\%; 8\%; and 10\% (v / v). A 50 mL CH\textsubscript{3}OH 25\% was added, then placed on a hotplate stirrer at 50 \(^\circ\)C and stirred for 24 hours. The mixture is filtered using a Buchner filter and washed with aquadest to neutral. 0.25 g of duck powder was subjected to an adsorption test on 100 ppm of Fe solution, by stirring using a magnetic stirrer for 100 minutes, then filtered using a Buchner filter. The results obtained were analyzed by Atomic Absorption Spectrophotometer (AAS-GBC Avanta \(\Omega\)) and analyzed by Fourier Transform Infrared (FTIR 8201PC Shimadzu, Japan) spectra of samples were recorded in a wide range of wave number from 400 to 4000 cm\(^{-1}\). Determination of adsorption capacity of Fe was carried out by mixing 0.25 g of sorbent with solutions at pH 5. Initial concentrations of metal solution varied from 100, 150,200, 250 and 300 ppm. The results obtained were analyzed by AAS and FTIR. The adsorption capacity is calculated using the Langmuir and Freundlich Isotherm equations.

**RESULTS AND DISCUSSION**

Adsorption of metal ions by fibrous materials such as keratin can be increased by treating it with a specific chemical, such as by the addition of HCl and CH\textsubscript{3}OH. Activation was performed by using 25% CH\textsubscript{3}OH and HCl solution which varied in concentration 2\%, 4\%, 6\%, 8\%, and 10\%. Activation of duck plum adsorbent aims to increase the number of ligands and form complexes with ferrous metal ions. The relationship between HCl concentration and percent iron was adsorbed by duck adsorbent shown in Fig-1. The decrease in the iron adsorption capacity of iron at concentrations above 4\% is due to the higher HCl concentration used, the more \(\text{H}^+\) ions that will surround the surface of the adsorbent so that the adsorbent becomes positively charged. In this case, metal ions which are also positively charged cause the rejection between the adsorbent surface with metal ions and the adsorption to become low. These excess \(\text{H}^+\) ions can damage the environmental conditions in the system, for example, keratin to be damaged and then dissolved in solution. Under acidic conditions, the amide is hydrolyzed, a nucleophilic attack will occur on the positive charge of the carbonyl oxygen, and cause the formation of tetrahedral intermediates I.

At equilibrium, tetrahedral I intermediates can form tetrahedral II intermediates. Reprotonation can occur either in oxygen or in nitrogen and form tetrahedral III intermediates. Protonation of nitrogen is more possible because the \(\text{NH}_2\) group is a stronger base than the \(\text{OH}\) group. In tetrahedral III intermediate compounds, there are two possible away groups, namely -OH and -\(\text{NH}_3\). The -\(\text{NH}_3\) group is a weaker base than the -\(\text{OH}\) group, making it easier to release and then to form carboxylic acid as the final product\textsuperscript{21}. The mechanism of hydrolysis of the amide in the acid solution can be seen in Fig-2.
Adsorption of Fe(III) onto Duck Feather

U. B. L. Utami et al.

Fig.-1: Graphic of the Concentration HCl Effect on the Absorbent Adsorption Capacity

Fig.-2: Mechanism of Amide Hydrolysis in Acid Solution

Esters are simply produced from the heating of carboxylic acids in an alcohol solution containing several strong acid catalysts. CH₃OH is chosen because it has the highest reactivity to the esterification reaction when compared with other types of alcohol. The reaction between keratin and CH₃OH can be seen as follows.

Fig.-3: The Reaction Scheme between Keratin and CH₃OH

Carboxylic acids present in keratin and CH₃OH solution undergo an esterification reaction and form an ester. However, the carboxylic acid is not sufficiently reactive to strike with the neutral alcohol condition, making it more reactive with the addition of HCl. Carboxylic groups act as ligands in the formation of complexes with metal ions. Fourier Transform Infrared Spectrophotometer is used to identify functional groups in duck scum before and after activation with 4% HCl and 25% CH₃OH, and duck adsorbents after contact with iron solution. FTIR spectra results can be seen in Fig-4.
According to Fig.-4, the FTIR spectra of duck feathers can be labeled as following Table-1.

Table-1: Functional Group Analysis on FTIR Spectra of Duck Finger Adsorbent before Activation, after Activation with 4% HCl-CH₃OH 25%, and after Fe Adsorption

<table>
<thead>
<tr>
<th>Adsorbent before Activation (cm⁻¹)</th>
<th>Adsorbent after Activation (cm⁻¹)</th>
<th>Adsorbent after Adsorption Fe (cm⁻¹)</th>
<th>Reference Wave Numbers (cm⁻¹)</th>
<th>Cluster Function Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3309.85</td>
<td>3294.42</td>
<td>3425.58</td>
<td>3000 - 3700</td>
<td>O-H</td>
</tr>
<tr>
<td>2276.00</td>
<td>2276.00</td>
<td>2337.72</td>
<td>2240 - 2350</td>
<td>S-H</td>
</tr>
<tr>
<td>1651.07</td>
<td>1651.07</td>
<td>1660.07</td>
<td>1500 - 1900</td>
<td>C=O</td>
</tr>
<tr>
<td>1527.62</td>
<td>1543.05</td>
<td>1533.25</td>
<td>1500 - 1650</td>
<td>N-H</td>
</tr>
<tr>
<td>1157.29</td>
<td>1157.29</td>
<td>1165.00</td>
<td>1000 - 1300</td>
<td>C-O</td>
</tr>
<tr>
<td>1234.44</td>
<td>1234.44</td>
<td>1242.16</td>
<td>900 - 1300</td>
<td>C-N</td>
</tr>
</tbody>
</table>

According to Table-1, the infrared spectrum of duck adsorbent showed absorption of 1651.07 and 1660.07 cm⁻¹ indicating the presence of a carboxylic acid group C = O. This is reinforced by the O-H vibration in 3309.85 cm⁻¹ and then there is a shift in 3294.42 cm⁻¹. In duck feather adsorbents that have been contacted with Fe solution, the O-H vibration occurs at 3425.58 cm⁻¹. S-H stretching vibration appeared at 2276.00 cm⁻¹ and then shifted to 2337.72 cm⁻¹. The bending N-H velocity of NH₂ appeared at 1527.62 cm⁻¹ then shifted to 1543.05 cm⁻¹. In the duck feather adsorbent that has been contacted with Fe solution, the bending N-H vibration appears at 1533.25 cm⁻¹. The C-O stretching of the ester appeared at 1527.62 cm⁻¹ and shifted to 1543.05 cm⁻¹. The C-N vibration gave the absorption at wavenumber 1234.44 cm⁻¹ and shifted to 1242.16 cm⁻¹. Alteration of the functional summits of the functional groups is suspected to have proved the interaction at the time of the activation process and when contacted with Fe metal solution. Keratin modified by Na₂S, the FTIR results showed that the carboxylic acid group in the sample was at wavenumbers 1261 and 1262 cm⁻¹. Amides at 3369 and 3376 cm⁻¹, and wavenumbers 2361 cm⁻¹ indicate the presence of amines²³. Keratin extraction with NaOH shows that the main structures of amide I, amide II and amide III are maintained, meaning that the peptide bond (~CONH) is not greatly affected in the process of base hydrolysis. At wave numbers 3265 cm⁻¹, there are OH and NH (amide A) stretches, and at 2916 cm⁻¹ is associated with symmetrical stretch CH₃ vibrations, while amide I is connected mainly to C=O stretch vibrations and occurs in the range (1700-1600 cm⁻¹)²⁴. Modification of keratin from chicken feathers using
methanol in an atmosphere acid showed that there was a change in peak sharpness at 1653 cm⁻¹ and a significant change at 1738 cm⁻¹ where esterification occurred in O of the carbonyl group, in the range of characteristic absorption (1750-1717 cm⁻¹).

This ligand will donate the free electron pairs and occupy the empty orbitals in the sub duster of the ferrous metal (central metal ion). Donation of ligand pairs of electrons to iron metal ions results in covalent coordination bonding. The possible scheme of Fe metal bond with keratin is shown in Fig.-5, like structure (an intrachain complex in wool keratin) could be formed if two carboxyl groups of two neighboring protein chains matched. Taking into account the expected value of such fragments frequency (50 per g of wool), Cu(II) uptake associated with the carboxylic residues can reach 150–300 μmoles/g of wool.

A possible scheme of the bonding of Fe metal with keratin is shown as follows.

![Fig.-5: Schematic Possibilities of Fe Metal Bond with Keratin](image)

To examine the relationship between sorbed ($q_e$) and aqueous concentration $C_e$ at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used. The linear form of the Langmuir is given by:

$$
\frac{C_e}{q_e} = \frac{1}{bK_L} + \frac{C_e}{b}
$$

(1)

Where $C_e$ is the equilibrium concentration of Fe(III) in solutions (mg/L), $b$ is the maximum uptake amount per g of adsorbent (mg/g), and $K_L$ is the Langmuir constant related to the binding energy of the sorption system (L/mg).

The linear form of the Freundlich isotherm is given by:

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

(2)

Where $K_F$ is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent and the constant $1/n$ indicates the adsorption intensity. A smaller value of $1/n$ implies stronger interaction between the adsorbent and heavy metal while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites.

The isotherm Langmuir and Freundlich of Fe ions by duck feather adsorbent before and after activation can be seen as follows (Fig.-6 and 7). Figure-6 and Fig.-7 show that Fe³⁺ adsorption in duck feathers follows both isotherms. The adsorption ion Fe³⁺ by adsorbent of duck feather follows the equation having the value of $R^2$ close to number 1. The result of the comparison of $R^2$ value indicates that the Langmuir and Freundlich isotherms equation has $R^2$ value close to 1. In duck adsorbent before activation is obtained $R^2$ value of 0.9379 for Langmuir isotherms and 0.9235 for Freundlich isotherms. While on duck feathers adsorbent after activation obtained value of $R^2$ equal to 0.9714 for isotherm Langmuir and 0.9648 for Freundlich isotherm. The Langmuir isotherm has a greater $R^2$ value and is closer to 1 when compared to Freundlich isotherms. This suggests that the duck's adsorbent surface is homogeneous and adsorb only one adsorbate molecule for each of its adsorbent molecules, as well as the Langmuir isotherm, in general, would be preferable to apply to chemical adsorption. Comparison of Langmuir and Freundlich isotherm constants obtained from other studies using other adsorbents shows that the adsorption of Fe by chitosan, Rice Hush ash (RHA), iron by fly ash from coal, acids-activated clays and kaolin based nanocomposite also followed both isotherms. On the biosorption of oil palm biomass Isotherm Langmuir> Temkin> Freundlich. The research of adsorption dye textile by father according to isotherm Langmuir and Freundlich are tantrasine and malachite green, azo dye amido black 10B, and azo dye brilliant yellow and textile dyes by hen feathers performed.
Adsorption of Fe(III) onto duck feather, methylene blue by feather keratin, and amoxicillin by chicken feather carbon, and reactive red 180 and reactive blue 21 by polyanilin CuCl$_2$ composite.

Fig.-6: (a) Langmuir Isotherm and (b) Freundlich Isotherm Adsorption of Fe$^{3+}$ Duck Feather Adsorbent before Activation

Fig.-7: (a) Langmuir Isotherm and (b) Freundlich Isotherm adsorption of Fe$^{3+}$ Duck Feather Adsorbent after Activation

To calculate the adsorbent adsorption capacity of modified HCl and CH$_3$OH duck feather obtained from the Langmuir Isotherm equation obtained from the relationship between Ce log and log qe. The results of the equation and the correlation coefficient ($R^2$) and the adsorption capacity (b) for the adsorption of Langmuir isotherms can be seen as follows.

Table-2: Data of Equations and Correlation Coefficients ($R^2$) for Adsorption of Langmuir Isotherms

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Equation</th>
<th>b (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before activation</td>
<td>$y = 0.009x + 0.1604$</td>
<td>111.11</td>
<td>0.9379</td>
</tr>
<tr>
<td>After activation</td>
<td>$y = 0.008x + 0.0326$</td>
<td>125.00</td>
<td>0.9714</td>
</tr>
</tbody>
</table>

Table-2 shows the graph of the relationship between Ce/me to the concentration of the iron solution so that the value of adsorption capacity for Fe$^{3+}$ ions by 25% CH$_3$OH and 4% HCl modified ducklings by 125.00 mg/g. These results indicate a high enough adsorption capacity, compared with previous studies conducted by chicken feather modified 6% CH$_3$OH and 2% HCl in As(III) only 0.13 mg/g$^{10}$. The other research results adsorption of copper with Dromaius novaehollandiae feathers and chitosan composite was an adsorption capacity of 18.78 mg/l$^{32}$. The adsorption of lead using biopolymer feather chicken on lead (Pb) of adsorption...
capacity was 1.9 g/l, and lead (Pb) adsorption by duck feather adsorption capacity was 2.3 g/l, and adsorption capacity of Methylene Blue by the chicken feather is 134.76 mg/g.

CONCLUSION
The conclusions that can be drawn from this research are the adsorption capacity of Fe by adsorbent of duck feather before and after activation with 4% HCl-CH$_2$OH 25% were 111.11 mg/g and 125.00 mg/g and the kinetics isotherm follows Langmuir and Freundlich isotherms

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