

Study of Duck Feather Modification using NaOH to Removal Iron in Acid Mine Drainage (AMD)

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Abstract. Study of duck feather modification using NaOH to removal iron in acid mine drainage (AMD) has been done. The objective of this study was to determine adsorption capacity. Modification duck feather that 2 g of duck powder was dissolved in 25 mL NaOH with a concentration of 1.00; 1.25; 1.50; 1.75; 2.00; and 2.25 % (v/v), 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 modification using NaOH optimum at concentration 1.50% and adsorption capacity before & after activation were 36.231 mg/g and 68.493 mg/g and potential to be used as an adsorbent to removal of Fe in acid mine drainage at coal mining.

Keywords. adsorption, Fe, duck feathers, NaOH, acid mine drainage

1. Introduction

The increase of duck breeding efforts can lead to increase generated hair waste. Based on data from the Livestock Service Office of South Kalimantan Province in 2014, 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 were used as adsorbents for absorbing metals and dyes in industrial wastewater. Related studies on chicken feathers included adsorbents as removal of Indigo Carmine dyes [1], as adsorbent with formic acid, to Methylene Blue, adsorption capacity of 134.76 mg/g [2] and adsorption research on Blue Astrazon 2RN textile dye (DBA) [3]. Modified chicken feathers with acylates for film and tested on textile waste [4] and Co(II) adsorption study by the protein grains produced from chicken feathers suggests that it is more efficient[5]. Research on adsorption of copper with *Dromaius novaehollandiae* feathers and chitosan composite that maximum adsorption was found 93.91% (18.78 mg/l) [6]. The adsorption of lead using biopolymer feather chicken on lead (Pb) of adsorption capacity was 1.9 g/L biosorbent. Lead adsorption (Pb) by duck feather adsorption capacity was 2.3 g /L [7]. The adsorption research of Pb²⁺, Cd²⁺ and Ni²⁺ by CH₃COOH modified

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chicken feathers and HCl showed that significant effect on adsorption of Pb^{2+} , for the desorption process had an effect on Pb^{2+} and Cd^{2+} , but not significant effect on Ni^{2+} [8]. Adsorption As (III) modified chicken feathers by NaOH, Na_2SO_3 , and CH_3OH showed that keratin from 6% CH_3OH and 2% HCl, CH_3OH higher when compared with the addition of NaOH and Na_2SO_3 , adsorption capacity 0.13 mg /g [9]. Research on chicken feathers as a metal absorber has been done with activation of Na_2S capable of absorbing Pb of 98.69%, duck feather composite with NaOH increased adsorption capacity on Cu^{2+} and Cr^{6+} [10], for that we need to do research for Fe ions which can later be applied for handling acid mine drainage (AMD), waste water in coal mining.

Coal mining has a negative impact, especially sulfuric acid formed from mining activities known as acid mine drainage (Widyati 2009). The results of acid mine water research conducted at PT. Jorong Barutama Greenstone (JBG) for Fe is 41.11 ppm, need metal handling, especially Fe. Coal mine acid water treatment conducted at PT. Jorong Barutama Greenstone (JBG) using phytoremediation of purun tikus (*Eleocharis dulcis*) has the ability to absorb Fe in the range of 26.92 to 91.76 mg/g, Mn from 0.0596 to 0.2364 mg/g [11]. Biological treatment using anaerobic processes can reduce sulfate by about 87% and iron [12]. The electrochemical method for processing AAT is the reduction of metals achieved in particular. Zn and Mn which reach 95-97%. [13]. Handling of Fe and Mn liquid wastes has been carried out, by electrocoagulation process [14]. Research on the adsorption of Fe (III) and Mn (II) by kayu apu (*Pistia stratiotes* L.) charcoal modified chitosan-glutaraldehyde, adsorption capacity of Fe(III) 1.011 mg/g [15], and Mn (II) 1.03 mg/g[16]. The treatment of acidic metal water by limestone in which 40 g of limestone is able to absorb Fe and Mn 95% and 82% in 200 ml acid mine drainage samples [17]. It becomes interesting to conduct the adsorption Fe on feather duck modified using NaOH to applied at acid mine drainage (AMD), waste water in coal mining.

2. Materials and Methods

2.1 Apparatus

The apparatus used in this study include a set of glassware, hotplate stirrer (STUART), analytical balance (OHAUS), oven (MEMMERT), blender, 40 mesh sieve, filter Buchner, magnetic stirrer, propipette, spool, Absorption Spectrophotometer Atom (AAS-GBC Avanta Ω) and Fourier Transform Infrared (FTIR 8201PC Shimadzu, Japan).

2.2 Materials

The materials used in this study include duck feather, detergent, petroleum ether pa, CH_3OH (99.90%, Merck), HCl (37%, Merck), NaOH (Merck), $FeCl_3 \cdot 6H_2O$ (Merck), HNO_3 (70%, Merck), mineral acid water, Whatman filter paper No. 42, and aquades.

2.3 Procedure

2.3.1 Preparation duck feather powder

One kg of duck feather is washed with water and detergent, then dried in the sun and the smell is gone, then heated with oven for 24 hours at 50 °C to remove the remaining water content. The duck feather is milled using a feather grinder and sieved using a 40 mesh sieve.

20 g of duck powder was soaked with 300 ml of 0.1 M HCl and 300 mL petroleum ether for 24 h, then washed with distilled water, then filtered using a Buchner filter. The obtained residue is dried with oven at 60 ° C. The results obtained were analyzed by FTIR.

2.3.2 Preparation of standard solution of Fe 100 ppm

1.21 g FeCl₃.6H₂O was dissolved with distilled water. The prepared solution is incorporated in a 250 mL measuring flask and aquades added to the boundary mark. Added 25 ml and diluted in a 250 mL measuring flask until the Fe 100 ppm solution was obtained.

2.3.3 Standard curves solution Fe

The raw curve is made by measuring the absorbance of the Fe solution. A total of 25 mL of 100 ppm standard solution was diluted in a 250 mL measuring flask until a Fe 10 ppm solution was obtained. 5; 10; 20; 30; 40 and 60 ml of Fe 10 ppm solution were diluted in 100 mL measuring flask until Fe solution was obtained at 0.5 ppm concentration; 1.0; 2.0; 3.0; 4.0; and 6.0 ppm (SNI 06-6989.4-2009).

2.3.4 Modification of duck feather adsorbents

2 g of duck powder was dissolved in 25 mL NaOH with a concentration of 1.00; 1.25; 1.50; 1.75; 2.00; and 2.25 % (v/v), then placed on hotplate stirrer at 50°C and stirred for 24 hours. The mixture is filtered using a Buchner filter and washed with aquadest to neutral. A total of 0.25 g of duck powder was done by adsorption test on Fe 100 ppm solution. The mixture is homogeneous 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 Ω) in Industry Research and Standardization Center Banjarbaru, South Kalimantan and analyzed by Fourier Transform Infrared (FTIR Perkin Elmer Model UATR) spectra of samples were recorded in a wide range of wave number from 400 to 4000 cm⁻¹ in Integrated Services Unit Laboratory Diponegoro University.

2.3.5 Determination of adsorption capacity of Fe by adsorbent duck feather

Fe solution of concentration 100, 150, 200, 250, and 300 ppm with pH 5. 50 mL Fe solution was pipetted into 5 provided erlenmeyer. A total of 0.25 g duck adsorbent is inserted into each erlenmeyer. The mixture was stirred using a magnetic stirrer for 100 minutes of contact time filtered using a Buchner filter. The results obtained were analyzed by AAS. The same procedure is performed on the adsorbent of duck that has not been activated. Furthermore, the adsorption capacity was calculated using the Langmuir isotherm.

2.3.6 Data analysis

The data obtained based on the parameters studied and made the graph to know the amount of adsorbed metal (M), obtained from the difference of concentration M before and after adsorption by duck modified adsorbent from the measurement of Atomic Absorption Spectrophotometer. The data is then incorporated into the equation:

$$\frac{C_e}{q_e} = \frac{1}{b.K_L} + \frac{C_e}{b} \quad (1)$$

Where:

q_e = Number of adsorbat adsorbed (mg / g)

C_e = Concentration of solution at equilibrium (ppm)

K_L = Langmuir constant from adsorption energy obtained from slope and intercept by plotting C_e / q_e to C_e

b = Maximum adsorption capacity (mg / g)

3. Results and Discussion

Duck feather waste is the main ingredient used in this study. 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 washing process, then proceed drying using oven to remove 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 mineral (deminceralization). The duck feather dander is filtered, then soaked with petroleum ether to remove the wax coating attached to the duck feather surface. The waxy coating on the duck feather can inhibit the process of adsorption of ferrous metal ions.

Adsorption of metal ions by fibrous materials such as keratin can be increased by treating it with a certain chemical, such as by adding NaOH. Modification carried out using a 1.25; 1.150; 1.75; 2.00; and 2.25. The modification of duck feather adsorbents aims to increase the number of ligands and form complexes with ferrous metal ions. The relationship between NaOH concentration and adsorption capacity of duck feather adsorbent is shown in Figure 1.

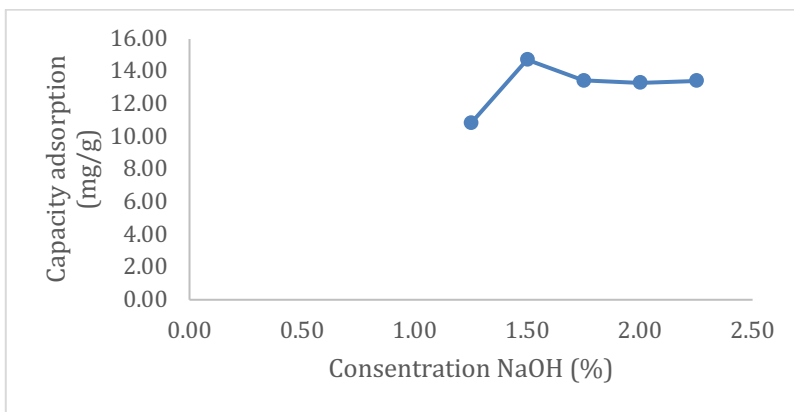


Figure 1. Relationship between concentration NaOH and Fe adsorption capacity

From the picture, it can be seen that at the NaOH concentration 1.50 % is highest of the adsorption capacity, and then stable until the concentration 1.75 to 2.25 %, indicating that the NaOH concentration is excessive, so it is no longer able to bind to keratin. The reaction that occurs between keratin and NaOH is estimated to be seen in Figure 2.

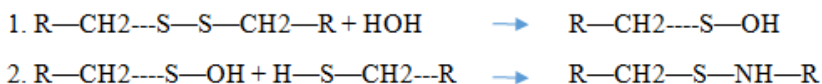


Figure 2. Reaction keratin with NaOH

Fourier Transform Infrared Spectrophotometer is used to identify functional groups keratin from duck feather before and after modification with NaOH and duck feather adsorbents after contact with Fe³⁺. FTIR spectra results can be seen in Figure 3.

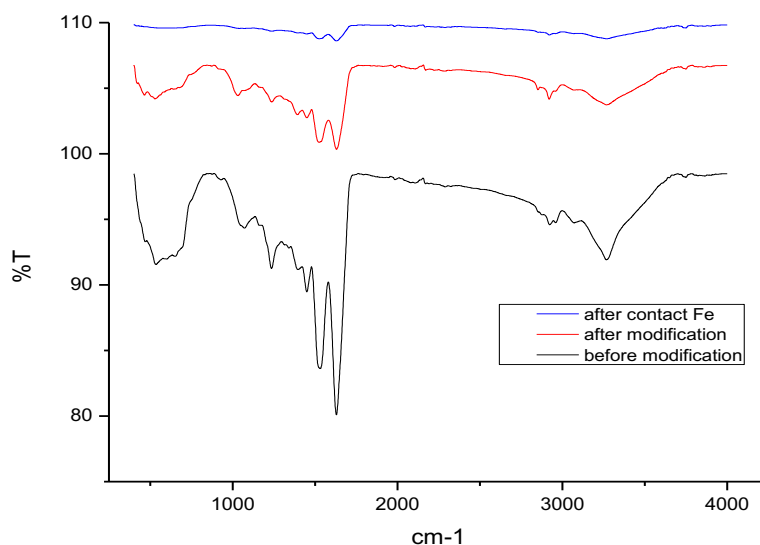


Figure 3. FTIR spectra of duck finger adsorbent (a) before modification, (b) after modification with NaOH and (c) after Fe³⁺ adsorption

Identify functional groups in FTIR spectra of adsorbent duck feathers before modification, after modification with NaOH, and after the adsorption process with Fe, showed in Table 1.

Table 1. Analysis of functional groups in FTIR spectra of adsorbent duck feathers before modification, after modification with NaOH, and after the adsorption process with Fe

Adsorbent Before modification (cm ⁻¹)	Adsorbent after modification (cm ⁻¹)	Adsorbent after the adsorption process with Fe (cm ⁻¹)	Reference Wave Numbers (cm ⁻¹)	Cluster Function Prediction
		3748.36		
3266.42	3266.22	3267.08	3000 - 3700	O-H
2922.50	2919.36	2920.90	2300-2700	S-H
		1982.47		
1629.27	1630.06	1629.14	1500 - 1900	C=O
1531.56	1523.99	1525.77	1500 - 1650	N-H
1450.01	1450.11		1340-1470	C-H
1396.09	1392.97			
1341.74				
1235.79	1237.06		1000 - 1300	C-O

According to Table 2, the infrared spectrum of duck adsorbent before modification shows 1629.27 cm⁻¹ absorption which indicates the presence of C=O carboxylic acid absorption. This is reinforced by the O-H vibration in the wave number 3266.42cm⁻¹. In duck feather

adsorbents that have been contacted with Fe solution, the O-H vibration occurs at a wave number of 3266.22 cm^{-1} . The S-H stretching vibration appeared at 2922.50 cm^{-1} . The bending N-H velocity of NH_2 appeared at 1531.56 cm^{-1} . In the duck feather adsorbent that has been contacted with Fe solution, the bending N-H vibration appears at the wave number 1523.99 cm^{-1} . The C-O stretching of the ester appeared at 1235.79 cm^{-1} and shifted to 1237.06 cm^{-1} [18]. The spectra results are in accordance with the functional groups of keratin because they show absorption of C-H, C-O, N-H₂ groups.

The FTIR spectrum of NaOH modified duck feathers is absorption bonds appear in 1392.97 cm^{-1} , 1317 cm^{-1} , and 1237.06 cm^{-1} absorption of hydrogen-bound NH groups (amide A, stretch NH), amide I (C=O stretch), amide II (flexible NH), amide III (CN stretching), and IV amide. Absorption bands appear at 1317 cm^{-1} , 1170 cm^{-1} , and 1124 cm^{-1} , which are associated with disulfide bonds in keratin and form SH [19]. Disulfide bonds (S-S) from are broken down thoroughly in the hydrolysis [20]. Keratin modified by Na_2S , the FTIR results showed that the carboxylic acid group in the sample was at wave numbers 1261 cm^{-1} and 1262 cm^{-1} . Amides at 3369 cm^{-1} and 3376 cm^{-1} , and at wave numbers 2361 cm^{-1} indicate the presence of amines [31]. Keratin extraction with NaOH shows that the main structures of amide I, amide II and amide III are maintained, meaning that the peptide bond ($-\text{CONH}$) 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 CH_3 vibrations, while amide I is connected mainly to C=O stretch vibrations and occurs in the range ($1700\text{--}1600\text{ cm}^{-1}$) [21]. Modification of keratin from chicken feathers using NaOH 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 ($1750\text{--}1717\text{ cm}^{-1}$) [9].

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 Figure 4, like structure in wool keratin could be formed if two carboxyl groups of two neighboring protein chains. 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 $150\text{--}300\text{ }\mu\text{moles/g}$ of wool. [22]

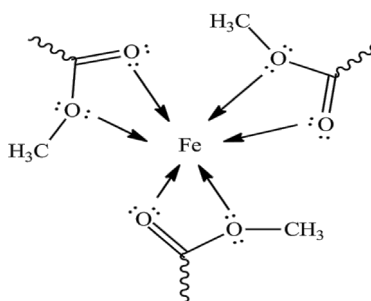


Figure 4. Schematic possibilities of Fe metal bond with keratin

Determination of adsorption isotherm model is done to know the process of adsorption of the iron metal ion by duck adsorbent modification with NaOH. The adsorption isotherm model used to describe the adsorption process on the solid surface with Langmuir isotherms. The adsorption capacity of Fe metal ions by duck adsorbent before and after modification is shown in Figure 5.

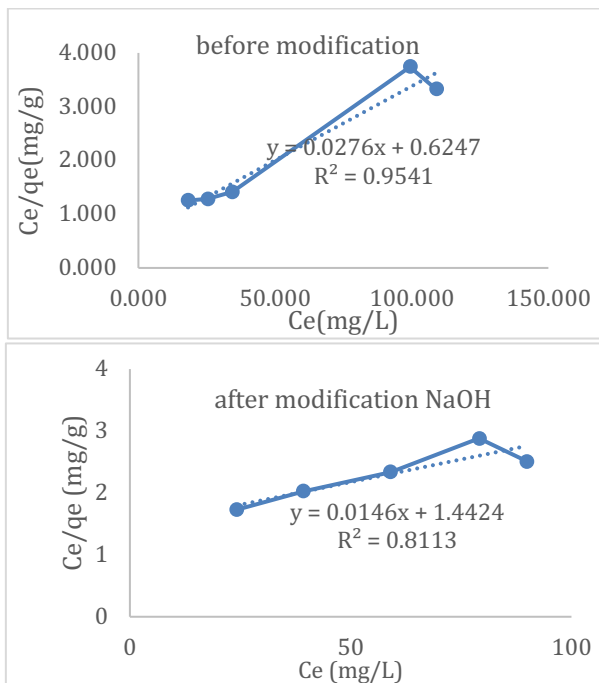


Figure 5. Langmuir isotherm adsorption of Fe duck feather adsorbent before and after modification NaOH

Figures 5 show that the adsorption of Fe on duck feather follows Langmuir and Freundlich isotherms. The adsorption ion of iron metal 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 have R^2 value close to 1. 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. The adsorption of Fe by chitosan [23], Rice Husk ash (RHA) [24] iron by fly ash from coal [25], and kaolinbased nanocomposite [26] also follows Langmuir and Freundlich isotherms. Isotherm Langmuir> Temkin>Freundlich biosorption iron using oil palm biomasses [27]. The research of adsorption dye textile by feather according 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 by [28][29]. Methylene blue by feather keratin [2], amoxicillin by chicken feather carbon [30], and Cd by modification of chicken feathers with ascorbic acid [31].

To calculate the adsorbent adsorption capacity of modified NaOH duck further obtained from Langmuir Isotherm equation. The results of the equation and the correlation coefficient (R^2) and the adsorption capacity (q_{max}) for the adsorption of Langmuir isotherms can be seen in Table 2.

Table 2. Data of equations and correlation coefficients (R²) for adsorption of Langmuir isotherms

Adsorbent	Equation	q _{max} (mg/g)	R ²
Before modification	y = 0.0276x + 0.6247	36.231	0.9541
After modification	y = 0.0146x + 1.4424	68.493	0.8113

Table 2 shows the graph of the relationship between Ce and Ce/qe to the concentration of the iron solution. so that the value of adsorption capacity for Fe³⁺ ions by NaOH modified duck further that 68.493mg/g. these results indicate a high enough adsorption capacity, and potential to be used as an adsorbent to overcome the problem of Fe in acid mine drainage (AMD) at coal mining . Compared with previous studies conducted. where the adapted capacity of the chicken feather is 6% CH₃OH and 2% HCl in As (III) only 0.13 mg/g [31]. The other research results adsorption of copper with *Dromaius novaehollandiae* feathers and chitosan composite. was 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 [7]. Adsorption of Methylene Blue by chicken feather with the adsorption capacity of 134.76 mg /g [33]. Maximum sorption capacity (q_{max}) values calculated from the Langmuir isotherm by chicken feather and magnetized activated carbon were 76.3, 56.5, 113.3, 32.6, and 45.5 respectively for Cd²⁺, Cu²⁺, Pb²⁺, Ni²⁺, and Zn²⁺, showing the suitability of the new sorbent for water and waste-water treatment usages [34]. The maximum adsorption capacities were ACF powder-hydrolyzed feathers (PHF) bio-modifier and *Trapa natans husks* (TH) are 50.2 mg/g for Cd(II) and 46.7 mg/g for Ni(II)) were higher than those of AC (33.8 mg/g for Cd(II) and 31.15 mg/g for Ni (II) [35]. The Langmuir isotherm model the maximum adsorption capacity of 76.92 and 83.33 mg/g for phenol and resorcinol respectively by Chitosan/Poly(acrylamide–Co-2-acrylamido-2-methyl-1- propanesulfonicacid) hydrogels [6].

4. Conclusion

The conclusions that can be drawn from this research are the adsorption capacity of Fe by adsorbent of duck feather before and after modification using NaOH were 36.231 mg/g and 68.493 mg/g and potential to be used as an adsorbent to removal of Fe in acid mine drainage (AMD) at coal mining.

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