



# Adsorption Iron Ions from Aqueous Solution onto Duck Feathers Modification using $\text{Na}_2\text{S}_2\text{O}_5$

U.B.L. Utami, H. Susanto<sup>1</sup>, B. Cahyono<sup>2</sup> and D. Ariyani

Chemistry Departement, Faculty of Mathematics and Sains, Lambung Mangkurat University Banjarmasin, Indonesia

<sup>1</sup>Chemical Department, Faculty of Engenering, Diponegoro University, Semarang, Indonesia

<sup>2</sup>Chemistry Department, Faculty of Mathematics and Sains, Diponegoro University, Semarang, Indonesia

E-mail: [umi.baroroh@ulm.ac.id](mailto:umi.baroroh@ulm.ac.id)

**Abstract:** Adsorption Iron Ions from Aqueous Solution onto Duck Feathers Modification using  $\text{Na}_2\text{S}_2\text{O}_5$  has been done. The objectives were to study modification reactions, to determine adsorption capacity. Modification duck feather adsorbents done by 2 g of duck powder was dissolved in 25 mL  $\text{Na}_2\text{S}_2\text{O}_5$  with a concentration of 0.025, 0.100, 0.175, 0.250, 0.325, 0.400 and 0.475M, then placed on hotplate stirrer at 50° C and stirred for 24 hours. The reaction mechanism was studied through functional group analysis using Fourier Transform Infrared (FTIR) spectroscopy. The results showed that adsorption capacity of Fe (III) by adsorbent of duck feather optimum with 3.25M and adsorption capacity before and after modification were 83.333 mg/g and 129.870 mg/g.

**Keywords:** Adsorption capacity, Iron, Duck feather,  $\text{Na}_2\text{S}_2\text{O}_5$

The increase of duck breeding efforts can lead to increase produce duck feather waste. Based on data from the Livestock Service Office of South Kalimantan Province in 2019, the number of ducks is 4,786,370 population, are generated can be estimated that a total of 239 tons of duck feather waste. These duck feather to be used as adsorbents for absorbing metals in industrial wastewater. Related studies on chicken feather modified with 6%  $\text{CH}_3\text{OH}$  and 2% HCl, adsorption capacity As(III) of 90,6 mg/g (Khosa, Wu and Ullah, 2013) and duck feathers on Fe(III) modified with 25%  $\text{CH}_3\text{OH}$  and 4% HCl adsorption capacity of 125 mg/g (Utami, Cahyono and Susanto, 2020). Duck feathers modified with NaOH have a relatively high concentration of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  adsorption capacity (Xiangyu Jin, Lu Lu, Haibo Wu, Qinfei Ke, 2013). The adsorption capacity of Pb by chicken feathers is 1.9 g/L and by duck feathers 2.3 g/L (Kumari and U. Kiran Babu 2011). Copper adsorption with *Dromaius novaehollandiae* feathers and chitosan composite maximum adsorption was found to be 93.91% (Kumari and Sobha 2015). Sodium sulfide is used as a less expensive chemical substitute for keratin extraction. Research on modification of keratin with  $\text{Na}_2\text{S}$  and immersion in isopropyl alcohol or weak acid (13 to 50% increase) or by crosslinking of formaldehyde or glutaraldehyde (24 to 40% increase) (Poole and Church 2015).  $\text{Pb}^{2+}$  ion adsorption using  $\text{Na}_2\text{S}_2\text{O}_5$  modified chicken feathers resulted in an adsorption capacity of 11.16 mg/g (Kong et al 2014). Cu adsorption on electroplating waste using modified NaOH/ $\text{Na}_2\text{SO}_3$  chicken feathers resulted in an adsorption capacity of 38.43 mg/g

(Sunarto 2014). Modification of keratin with sodium metabisulfite showed that the optimum level was 0.2 M with a yield of 87.6% (Ji et al 2014).

Previous research on the reaction mechanism of keratin using sodium sulfide includes the extraction of keratin from wool through sulfitolysis, with the formation of cysteine (R-S-H) (Aluigi et al 2014). The results of studies of keratin from rabbit hair showing typical absorption at 3420, 1650, 1543, 1240, and 685  $\text{cm}^{-1}$ , showing NH(II), amide III (CN) and amide IV, respectively (Wang et al 2018). The results of another study showed the presence of disulfide bonds in keratin and formed SH (Zhang et al 2013) and disulfide bonds (S-S) from being completely broken down in hydrolysis (Hamouche et al 2018). For this reason, it is necessary to conduct research on the modification of keratin from duck feathers using  $\text{Na}_2\text{S}_2\text{O}_5$  and study the reaction mechanism and study its adsorption.

## MATERIAL AND METHODS

**Preparation duck feather powder:** One kg of duck feather is washed with detergent and water, 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 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.

**Modification of duck feather adsorbents:** 2 g of duck

powder was dissolved in 25 mL  $\text{Na}_2\text{S}_2\text{O}_5$  with a concentration of 0.025; 0.100; 0.175; 0.250; 0.325; 0.400; and 0.475M, then placed on hotplate stirrer at  $50^\circ\text{C}$  and stirred for 24 hours. The mixture is filtered using a Buchner filter and washed with distilled water 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, and then filtered using a Buchner filter. The results obtained were analyzed by Atomic Absorption Spectrophotometer (AAS-GBC Avanta  $\Omega$ ) in Industry Research and Standardization Center Banjarbaru, South Kalimantan and analyzed by Fourir Fourier Transform Infrared (FTIR 8201PC Shimadzu, Japan) spectra of samples were recorded in a wide range of wave number from 400 to  $4000\text{ cm}^{-1}$  in Laboratory of Organic Chemistry and Biochemistry Department of Chemistry, Gadjah Mada University.

**Determination of adsorption capacity of Fe by adsorbent duck feather:** Fe solution of concentration 100, 150, 200, 250, and 300 ppm with pH 6. 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 Atomic Absorption Spectrophotometer (AAS-GBC Avanta  $\Omega$ ) in Industry Research and Standardization Center Banjarbaru, South Kalimantan the same procedure is performed on the adsorbent of duck that has not been activated. Furthermore, the adsorption capacity was calculated using the Langmuir and Freundlich Isotherm.

**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:

**Ishoterm Langmuir**

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

where,  $q_e$  = the amount adsorbed per unit weight of adsorbent ( $\text{mg.g}^{-1}$ )  $C_e$  = the equilibrium concentration ( $\text{mg.L}^{-1}$ )  $K_L$  = the Langmuir adsorption constant, indicating the binding energy between adsorbent and adsorbate ( $\text{L.mg}^{-1}$ )  
 $b$  = Maximum adsorption capacity ( $\text{mg.g}^{-1}$ )

**Ishoterm Freundlich**

$$\text{Log } q_e = \text{log } KF + 1/n \text{ log } C_e \quad (2)$$

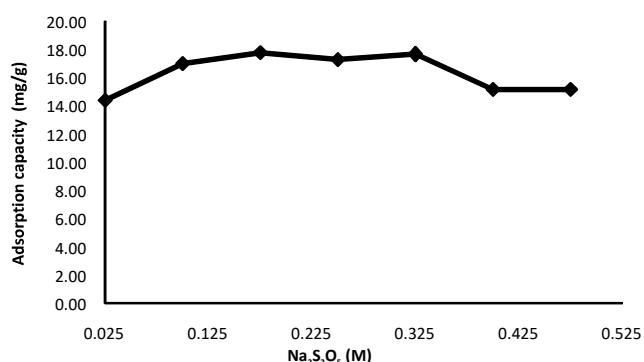
where,  $q_e$  = Number of adsorbat adsorbed ( $\text{mg.g}^{-1}$ )  
 $C_e$  = Concentration of solution at equilibrium ( $\text{mg.L}^{-1}$ )  
 $KF$  and  $1/n$  = Freundlich constants of the adsorbent adsorption capacity and intensity.

## RESULTS AND DISCUSSION

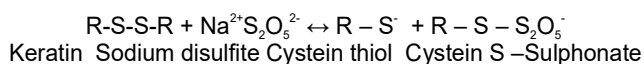
Adsorption of metal ions by fibrous materials such as keratin can be increased by treating it with a certain chemical, such as by adding  $\text{Na}_2\text{S}_2\text{O}_5$ . Activation is carried out using a 0.025; 0.100; 0.175; 0.250; 0.325; 0.400; and 0.475M. The activation of duck feather adsorbents aims to increase the number of ligands and form complexes with ferrous metal ions. The relationship between  $\text{Na}_2\text{S}_2\text{O}_5$  and adsorption of duck feather adsorbent is shown in Figure 1.

From the picture, it can be seen that at the  $\text{Na}_2\text{S}_2\text{O}_5$  concentration after 0.175M the condition of the adsorption capacity is stable until the concentration is 0.325M. At a concentration of .400, this begins to decrease, indicating that the  $\text{Na}_2\text{S}_2\text{O}_5$  concentration is excessive, so it is no longer able to bind to keratin. The reaction that occurs between keratin and  $\text{Na}_2\text{S}_2\text{O}_5$  is estimated to be seen in Figure 2, where cysteine thiol and S-sulfonation residues will occur. Sodium sulfite ( $\text{SO}_3^{2-}$ ), bisulfite ( $\text{HSO}_3^-$ ), and sulfite ( $\text{S}_2\text{O}_5^{2-}$ ) are the main sulfite compounds present in aqueous solutions and can be used for sulfitolysis. First, hydrosulfite and hydroxyl ions are formed from the reaction of sodium sulfite with water in Figure 4. In the next step, hydroxyl ions break disulfide bonds and form dehydroalanin and perthiocysteine as a propops (Poole and Church 2015).

The dehydroalanin formed from this reaction is very reactive and forms lanthionin and lysinoalanine through a cross linking with cysteine and lysine (Fig. 6). This cross-linking reaction can improve the mechanical properties of the final regeneration product, however, sodium sulfite treatment can damage the backbone of proteins, and therefore, optimizing the extraction conditions is an important step to maintain the structure of keratin (Shavandi *et al.*, 2008). Thiol



**Fig. 1.** Relationship between  $\text{Na}_2\text{S}_2\text{O}_5$  concentration and Fe adsorption capacity



**Fig. 2.** Sulfitolysis cystin reaction by sulfite

groups (-SH) play a definite role during the grafting of the Monomer methyl Acrylate (MMA) onto the wool by providing sites for grafting. Thiol groups present on the cysteine aminoacids have been reported as the preferred sites for grafting monomers by some researchers. (Shavandi and Ali 2019). Fourier Transform Infrared Spectrophotometer is used to identify functional groups keratin from duck feather before and after modification with  $\text{Na}_2\text{S}_2\text{O}_5$ , and duck feather adsorbents after contact with  $\text{Fe}^{3+}$ . FTIR spectra results can be seen in Figure 7. Identify functional groups in FTIR spectra of adsorbent duck feathers before modification, after modification with  $\text{Na}_2\text{S}_2\text{O}_5$ , and after the adsorption process with Fe, showed in Table 1.

Based on Table 1, the infrared spectrum of the duck feather before modification shows an absorption of  $3266\text{ cm}^{-1}$  indicating a symmetrical OH stretching vibration range of NH, strengthened by the presence of buckling  $\text{N}_2\text{H}$  which absorbs near  $1531\text{ cm}^{-1}$ , SH stretching vibrations appear at  $2276\text{ cm}^{-1}$ ,  $1629\text{ cm}^{-1}$  which marks the absorption of C=O carboxylic acid, Absorption  $1235\text{ cm}^{-1}$  marks the stretching vibration of CO carboxylic acid and  $1072$  which marks CN, Based on the results of FTIR spectra it can be concluded that in duck feathers there are keratin groups, similar to research on chicken feathers and rabbit fur (Sa'adah N, R. Hastuti 2013), (Wang et al 2018).

Infrared spectrum of duck feather after modification shows  $1618.80\text{ cm}^{-1}$  absorption which indicates the presence of C=O carboxylic acid absorption. This is reinforced by the O-H vibration in the wave number  $3266.17\text{ cm}^{-1}$ . The FTIR spectra of the  $\text{Na}_2\text{S}_2\text{O}_5$  modified duck feathers are in agreement with the results of keratin studies from rabbit hair

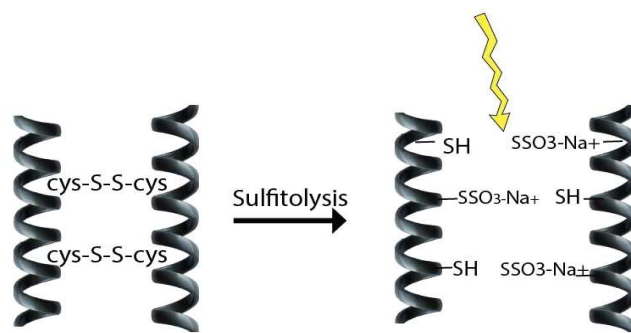


Fig. 3. Schematic diagram of the sulfitolysis reaction which breaks the strong disulfide bonds of keratin fibers

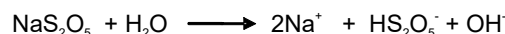


Fig. 4. Reaction of the formation of hydroxyl and hydroxyl ions from the reaction of sodium disulfite with water

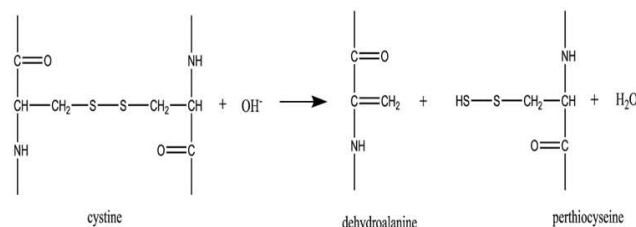


Fig. 5. Hydroxyl ion reaction breaks dehydroalanine sulfite bonds

Table 1. Analysis of functional groups in FTIR spectra of adsorbent duck feathers before modification, after modification with  $\text{Na}_2\text{S}_2\text{O}_5$ , and after the adsorption process with Fe

Adsorbent before modification ( $\text{cm}^{-1}$ )	Adsorbent after modification ( $\text{cm}^{-1}$ )	Adsorbent after the adsorption process with Fe ( $\text{cm}^{-1}$ )	Reference wave numbers ( $\text{cm}^{-1}$ )	Cluster function prediction
3266.42	3265.17	3273.98	3000 - 3700	O-H
2276.00	2276.00	2337.72	2300-2700	S-H
		2108.64		
1629.27	1618.80	1630.65	1500 - 1900	C=O
1531.56	1536.03	1522.60	1500 - 1650	N-H
1450.01	1448.21	1448.03	1340-1470	C-H
1396.09				
1341.74	1229.26			
1235.79	1201.46	1229.81	1000 - 1300	C-O
	1159.60			
	1077.52			
1072.32	1023.44	1023.32	900 - 1300	C-N

showing typical absorption at 3420, 1650, 1543, 1240, and 685  $\text{cm}^{-1}$ , showing NH(II), amide III (CN) and amide IV (Wang et al 2018). The results of keratin studies from rabbit hair showing characteristic absorption at 3420, 1650, 1543, 1240, and 685  $\text{cm}^{-1}$ , respectively showing NH(II), amide III (C-N) and amide IV. Keratin modified with a deep eutectic solvent (DES) mixture of choline chloride and oxalic acid shows the absorption of amide I, which may be associated with lower amounts of  $\alpha$ -helical crystallites. In addition, new weak absorption bands appear in 1317, 1170, and 1124  $\text{cm}^{-1}$  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, 1170, and 1124  $\text{cm}^{-1}$ , which are associated with disulfide bonds in keratin and form SH (Zhang et al 2013) Disulfide bonds (S-S) from are broken down thoroughly in the hydrolysis. Keratin modified by  $\text{Na}_2\text{S}$ , the FTIR results showed that the carboxylic acid group in the sample was at wave numbers 1261 and 1262  $\text{cm}^{-1}$ . Amides at 3369 and 3376  $\text{cm}^{-1}$ , and at wave numbers 2361  $\text{cm}^{-1}$  indicate the presence of amines (Yilmaz et al 2019). 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 (Hamouche et al 2018). At wave numbers 3265  $\text{cm}^{-1}$ , there are OH and NH (amide A) stretches, and at 2916  $\text{cm}^{-1}$  is associated with symmetrical stretch  $\text{CH}_3$  vibrations, while amide I is connected mainly to C=O stretch vibrations and occurs in the range (1700-1600  $\text{cm}^{-1}$ ). Modification of keratin from chicken feathers using methanol in an atmosphere acid showed that there was a change in peak sharpness at 1653  $\text{cm}^{-1}$  and a significant change at 1738  $\text{cm}^{-1}$  where esterification occurred in O of the carbonyl group, in the range of characteristic absorption (1750-1717  $\text{cm}^{-1}$ ) (Khosa, Wu and Ullah, 2013).

In duck feather adsorbents that have been contacted with Fe solution, the O-H vibration occurs at a wave number of 3425.58  $\text{cm}^{-1}$ . The S-H stretching vibration appeared at 2276.00  $\text{cm}^{-1}$ . The bending N-H velocity of  $\text{NH}_2$  appeared at 1531.56  $\text{cm}^{-1}$ . In the duck feather adsorbent that has been contacted with Fe solution, the bending N-H vibration appears at the wave number 1522.60  $\text{cm}^{-1}$ . The C-O stretching of the ester appeared at 1159.60  $\text{cm}^{-1}$  and shifted to 1235.79  $\text{cm}^{-1}$ . The C-N vibration gave the absorption at wave number 1023.32  $\text{cm}^{-1}$  and shifted to 1072.32  $\text{cm}^{-1}$ . Alteration of the functional summits of the functional groups is suspected to have proved the interaction at the time of the amodification process and when contacted with  $\text{Fe}^{3+}$ . 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 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  $\mu\text{moles/g}$  of wool (Nikiforova, Kozlov and Islyaikin 2019).

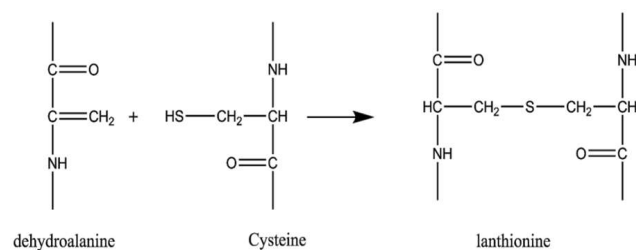


Fig. 6. Arrangement of lanthioalanin by the addition of cysteine to dehydroalanin

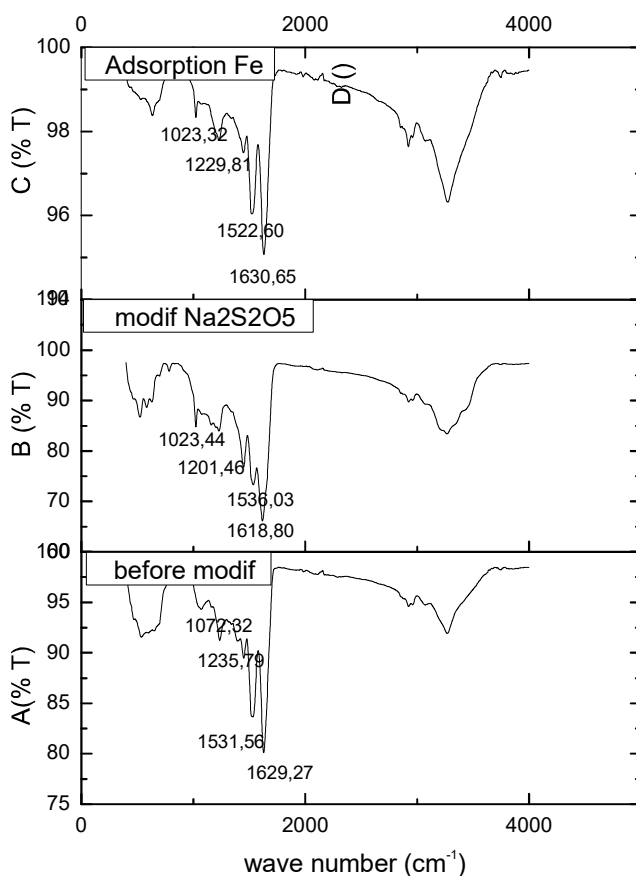


Fig. 7. FTIR spectra of duck finger adsorbent (A) before modification, (B) after modification with  $\text{Na}_2\text{S}_2\text{O}_5$  and (C) after  $\text{Fe}^{3+}$  adsorption

Determination of adsorption isotherm model is done to know the process of adsorption of the iron metal ion by duck adsorbent modification with  $\text{Na}_2\text{S}_2\text{O}_5$ . The adsorption isotherm model used to describe the adsorption process on the solid surface, Langmuir and Freundlich isotherms. The adsorption capacity of Fe metal ions by duck adsorbent before and after modification is shown in Figure 9 and 10.

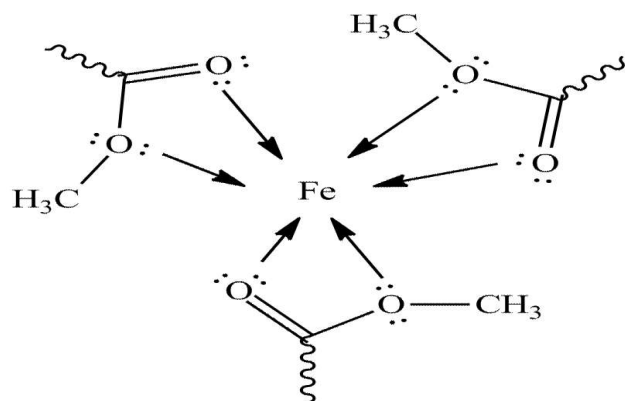


Fig. 8. Schematic possibilities of Fe metal bond with keratin

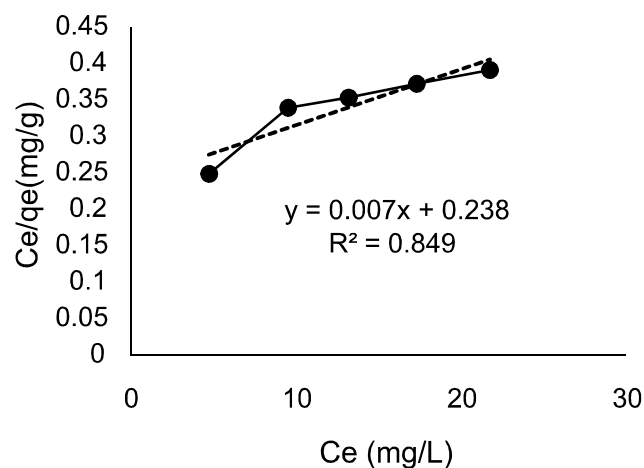
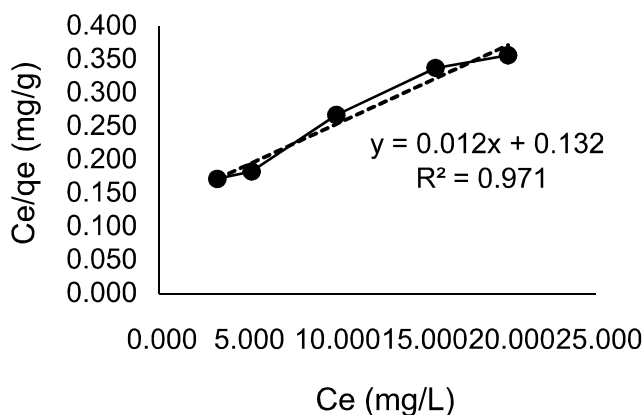


Fig. 9. Langmuir isotherm adsorption of Fe duck feather adsorbent before and after modification  $\text{Na}_2\text{S}_2\text{O}_5$

Figures 9 and 10 shows 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 (Radnia, Ghoreyshi and Younesi, 2011), Rice Hush ash (RHA) (Zhang et al 2014) iron by fly ash from coal (Irawan and Rumhayati 2014), and kaolin based nanocomposite (Shaban, Hassouna and Nasief, 2017) also follows Langmuir and Freundlich isotherms. Isotherm Langmuir > Temkin > Freundlich biosorption iron using oil palm biomasses (Khosraviahftkhany and Morad 2013). The research of adsorption dye textile by father 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 (Mittal, Thakur and Gajbe 2012) (Mittal, Thakur and Gajbe 2013). Methylene

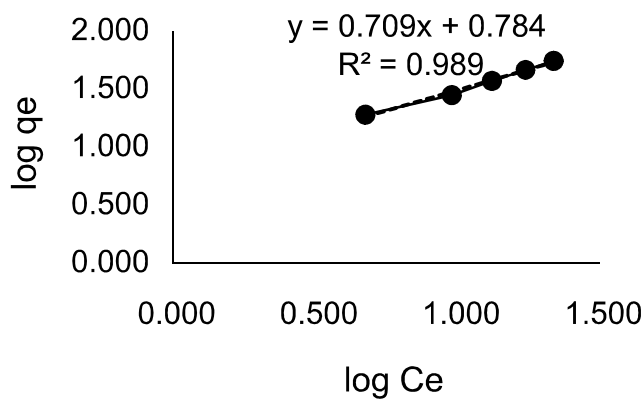
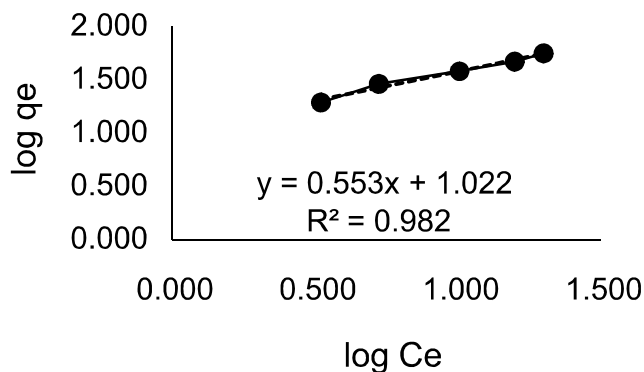


Fig. 10. Freundlich isotherm adsorption of Fe duck feather adsorbent before and after modification  $\text{Na}_2\text{S}_2\text{O}_5$

**Table 2.** Data of equations and determination coefficients ( $R^2$ ) for adsorption of Langmuir isotherms and Freundlich isotherms

Adsorbent	Isotherm Langmuir Equation	$q_{max}$ (mg/g)	$R^2$
Before modification	$y = 0.012x + 0.1323$	83.333	0.972
Modification $Na_2S_2O_5$	$y = 0.0077x + 0.2383$	129.870	0.849

blue by feather keratin (Chowdhury and Saha 2012a), amoxicillin by chicken feather carbon (Li et al 2017). To calculate the adsorbent adsorption capacity of modified  $Na_2S_2O_5$  duck further obtained from Langmuir and Freundlich isotherm equation obtained from the relationship between  $C_e$  log and log  $q_e$ . The results of the equation and the determination coefficient ( $R^2$ ) and the adsorption capacity ( $q_{max}$ ) for the adsorption can be seen in Table 2.

Table 2 shows the graph of the relationship between  $C_e/q_e$  to the concentration of the iron solution. so that the value of adsorption capacity for  $Fe^{3+}$  ions by  $Na_2S_2O_5$  modified duck further that 129.870 mg/g. Compared with previous studies conducted. Where the adapted capacity of the chicken feather is 6%  $CH_3OH$  and 2%  $HCl$  in As (III) only 96.00 mg/g (Khosha, Wu and Ullah, 2013). The other research results adsorption of copper with *Dromaius novaehollandiae* feathers and chitosan composite. was adsorption capacity of 18.78 mg/l (Kumari and Sobha, 2015). 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 (Kumari and Babu 2011). Adsorption of Methylene Blue by chicken feather with the adsorption capacity of 134.76 mg/g (Chowdhury and Saha, 2012b). Maximum sorption capacity ( $q_{max}$ ) by chicken feather and magnetized activated carbon were 76.3, 56.5, 113.3, 32.6, and 45.5 respectively for  $Cd^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$ , showing the suitability of the new sorbent for water and waste-water treatment usages (Rahmani-sani et al 2020). 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) (Yin et al 2019).

## CONCLUSIONS

Analysis of keratin from duck feathers using  $Na_2S_2O_5$  showed that keratin had formed which was indicated by a shift in wavenumber in the FTIR spectrum. Adsorption capacity of Fe(III) by adsorbent of duck feather modified with  $Na_2S_2O_5$  optimum with 3.25M and adsorption capacity before & after modification were 83.333 mg/g and 129.870 mg/g. Adsorption of Fe on duck feather modified with  $Na_2S_2O_5$

follows Langmuir and Freundlich isotherms. Duck feathers that have been modified with  $Na_2S_2O_5$  can be used as adsorbents in wastewater containing heavy metals

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