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Adsorption capacity test of $Na_2S_2O_5$ modified duck feather high density polyethylene (HDPE) composite in Mn solution continuously

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ABSTRACT

One of the poultry businesses that is developing in Indonesia is duck farming. Duck farming has a relatively smaller risk, so it has great potential for development. One solution that is being developed is the use of keratin contained in duck feathers as an adsorbent that can be used to reduce metal levels. This research aims to determine the optimum volume and adsorption capacity required in the manganese ion adsorption process. The optimum volume and manganese adsorption capacity were measured using Atomic Absorption Spectrophotometer (AAS) to determine the amount of manganese ions that were adsorbed with the duck feather keratin-$Na_2S_2O_5$- HDPE composite adsorbent. Determination of the optimum volume is carried out with volume variations of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 liters, while determining Adsorption capacity was carried out using a 100 ppm manganese solution flowed at a speed of 0.2 liters/minute. The results of this research show that the optimum conditions for manganese ion adsorption occur at a volume of 1.2 liters of 82.248 mg/L and an adsorption capacity of 17.029 mg/g. The conclusion of this research is that HDPE duck feather composite can absorb mn metal ions, where the resulting adsorbent will have strong adsorption capacity and can bind metal ions.

1. Introduction

The contamination of water resources with heavy metal and chemical compounds has emerged as a pressing environmental challenge in recent years [1-3]. Heavy metals are one of the most important contaminants in water and soil. Heavy metals are discharged into the environment by several industries, such as mining, metallurgy, electronics, electroplating and metal finishing. The removal of heavy metals from wastewater tends to accumulate in living organisms. In addition, heavy metals cannot be degraded or destroyed [4]. Manganese is one of three important elements that is toxic if it has too high a concentration in the body, but it is also needed by humans to survive. Contamination with manganese (Mn) was found. The environmental problem of Mn in river water can be a hundredfold increased by anthropogenic enrichment.

This prosess a problem because Mn easily bioaccumulates, which can cause undesirable ecotoxicological effects, and in the case of long-term exposure to Mn and high doses of its compounds, it causes adverse effects on human health [5]. Excessive Mn in water or soil may pose ecological and health risks. Indeed, studies have documented that pollution with Mn and other heavy metals often stems from anthropogenic activities mining, coal extraction, metal smelting, industrial discharges, and waste from mining processing as well as from natural geogenic sources [6]. Wastewater from coal-mining operations has been found to contain Mn and other heavy metals above environmental quality standards [7], groundwater contamination with Mn and iron has been reported in mining regions, where concentrations greatly exceed safe drinking-water thresholds aising concerns over long-term human health effects [8]. The toxicological concerns associated with Mn are serious, excessive Mn exposure has been linked to neurotoxic effects. Overaccumulation of Mn in the central nervous system may trigger neurological disorders; ingestion over time can subtly alter

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neurochemistry and cognitive functions [9].

One way to remove contaminants is by adsorption. To remove heavy metal contamination, many studies have been conducted, including the adsorption of Pb using Fava Bean Pods [10]. The adsorption of organic fluorine compounds from aqueous solutions [11] . The removal of Pb(II) using cellulose extracted from *Pentaclethra macrophylla* Benth pod [12].

The use of iron oxide nanoparticles synthesized from *Acacia nilotica* leaves for the sequestration of several heavy metals [13] and the adsorption of fluoride ions onto hydroxyapatite-modified *Corbula trigona* shell waste [14]. The other research related to adsorption has been carried out extensively [15-19]. Experts already know that fibrous materials such as wool, chicken feathers and hair can adsorb metal ions in solution [20].

Pb^{2+} ion adsorption research using $Na_2S_2O_5$ modified chicken feathers resulted in an adsorption capacity of 11.16 mg/g [21]. Keratin from duck feathers modified with $Na_2S_2O_5$ which is absorbed with Fe(III) has an adsorption capacity of 129,870 [22]. and modification with CH_3OH has an adsorption capacity of 125 mg/g [23]. Ducks are one type of poultry that is widely cultivated by the people of South Kalimantan. Duck feathers as a composite material contain around 91% keratin protein which can potentially be used into high-value compounds or products because it consists of keratin protein or keratin fiber. The flexible nature of keratin and having lots of fibers can be used to make strong products or materials [24].

Keratin contains functional groups such as sulphihydral groups (S-H), carboxyl groups (–COOH) and amine groups (-NH_2) which can act as active sites in the heavy metal adsorption process [23]. Study Pb^{2+} ion adsorption using $Na_2S_2O_5$ modified chicken feathers resulted in an adsorption capacity of 11.16 mg/g [21], the adsorption capacity of Pb by chicken feathers (1.9 g/L) was lower than that of duck feathers (2,3 g/L)[25]. Keratin from chicken feathers modified with 6% CH_3OH and 2% HCl on As adsorption had an adsorption capacity of 90.6 mg/g [26]. Adsorption model with two binding sites was used to calculate steric and energy parameters of the adsorption of $Pb^{2+,}$ Cd^{2+} and Ni^{2+} on chicken feathers [27]. Duck feathers activated with NaOH have a relatively high concentration of Cu^{2+} and Cr^{6+} adsorption capacity [28]. Keratin from chicken feather can be prepared into membrane [29], hydrogel [30], fiber [31-32], and the modification has focused on using polymer grafting or compositing [33]. The use of poultry feathers as a metal absorber has a disadvantage, namely that it is very small in size, and can only be used once. In order for the adsorbent from poultry feathers to have high mechanical resistance and can be used repeatedly, one way is to make it composite with other materials.

Research into the manufacture of composites with keratin from bird feathers using plastic has been widely carried out, including using Low Density Polyethylene (LDPE) LDPE [[34], Linear Low Density Polyethylene LLDPE [35] and Polyvinyl Choride-High Density Polyethylene (PVC- HDPE) [36]. The manufacture of ensete fiber composites with maleic anhydrous and HDPE showed that the addition of ensete fiber resulted in a stiffer and harder composite which caused a decrease in elongation at break.

The addition of 5 wt% maletic anhydride compatibilizer to 25 wt% HDPE ensete fibers increased fiber-matrix adhesion [37]. The manufacture of bagasse fiber composites with HDPE showed that the highest tensile strength was obtained in the composition of HDPE plastic and bagasse fiber by volume of 60%: 40% with an average value of 15.5 MPa, while the highest bending strength was obtained in the composition of HDPE plastic and bagasse fiber by volume. 60% : 40% with a mean value of 16.8 MPa [38].

The $Na_2S_2O_5$ duck feather composite with HDPE on continuous absorption of Fe^{3+} showed that the adsorption capacity was 93.302 mg/g [39]. For this reason, it is necessary to carry out research on continuous Mn adsorption.

2. Materials and Methods

2.1. Materials and tools

The materials used in this study include duck feather, detergent, petroleum ether pa, $Na_2S_2O_5$ (Merck), HCl (37%, E.Merck), NaOH (E.Merck), $FeCl_3.6H_2O$ (E.Merck), HNO_3 (70%, E. Merck), xylem (E. Merck), benzoyl peroxide (E. Merck), anhydrous maleic acid (E. Merck), mineral acid water, Whatman filter paper No. 42, and aquades. The tools used in this study includes 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) and Scanning Electron Microscope (SEM).

2.2. Preparation of modified $Na_2S_2O_5$ duck feather composite with HDPE

This composite was made for duck feathers with 0.325M $Na_2S_2O_5$and continued by varying the percentage between HDPE polyethylene and duck feathers at 10:90; 20:80; 30;70, 60:40 and 50:50. HDPE polyethylene was dissolved using xylen and benzoyl peroxide and anhydrous maleic acid were added at a temperature of 145^{o}C and duck feathers were added which had been activated with 0.325M $Na_2S_2O_5$. While stirring until blended, then molded to form pellets while still hot. The sample was analyzed for functional groups using FTIR and surface analysis using SEM.

2.3. Determination of adsorption capacity of duck feather composite -$Na_2S_2O_5$-HDPE in Mn^{2+} solution continuously

The modified duck feather composite was placed in a cylindrical tube made of glass with a composite weight of about 4 grams, with a flow rate of 200 ml/min. The bottom and top are given a sponge/foam to hold the incoming water and to hold the adsorbent.

The bottom is also given a faucet to drain water with a concentration of iron (Fe) 100 ppm. Water flow measurements were carried out for every 200 ml. A schematic figure of a continuous composite adsorption capacity test can be seen in the following figure. To calculate the adsorption capacity of the adsorbent continuously, the Thomas equation is used (Figure 1).

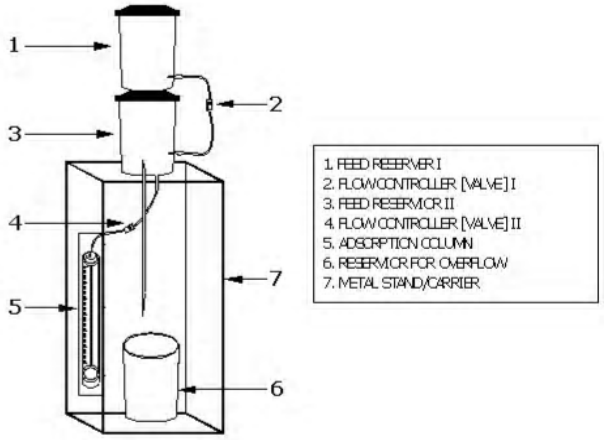


Fig. 1. Schematic diagram of Experimental filtration test

2.4. Data analysis

To calculate the adsorption capacity of the dynamic system, it is calculated using the Thomas model equation [40-48].

$$\ln\left[\frac{Co}{Ce}-1\right]=\frac{KTh.qo.M}{Q}-\frac{KTh.Ce}{Q}Veff \quad (1)$$

Where, Co = influent concentration (mg/L), Ce = effluent concentration (mg/L), KTh = Thomas rate constant (mL/min.mg), qo = adsorption capacity (mg/g), Q = influent flow rate (mL/min), M = mass of adsorbent (g), Veff = effluent volume (L)

$$y = \ln\left[\frac{Co}{Ce}-1\right]$$

x = Veff

This is similar to the equation of a line:

y = ax + b, Slope a = $\frac{KTh.Ce}{Q}$, Intercept b = $\frac{KTh.qo.M}{Q}$

$$qo=\frac{b.Q}{KTh.M} \quad (2)$$

3. Results and Discussion

3.1. Duck Feather Adsorbent

Duck feather waste is the main material used in this study. Duck feathers are washed thoroughly to remove dirt attached to the duck feathers, then dried under sunlight to remove water content after the washing process, then continued drying using an oven at a temperature of 60 ° C to remove the remaining water content. Duck feathers are cut, then ground using a feather grinding machine and sieved with a size of 40 mesh to increase the surface area of duck feather powder. The fine duck feather powder is soaked with petroleum ether to remove the wax layer attached to the surface of the duck feathers. Furthermore, it is washed using distilled water and dried in an oven at a temperature of 70° C to remove the remaining petroleum ether and obtain duck feathers that will be used.

3.2. Modification of duck feather $Na_2S_2O_5$ and HDPE polyethylene

Modification of duck feathers with $Na_2S_2O_5$ aims to change the keratin structure to be more easily degraded so that it can obtain adsorption capacity on duck feather keratin. After being washed and dried using an oven, the next stage is the activation process carried out with a 0.35 M $Na_2S_2O_5$ solution. The function of $Na_2S_2O_5$ in this process is as a reduction reagent that breaks the disulfide bonds in keratin, so that the bond structure can become looser or the cross-linking of keratin can be reduced. The results of the study of duck feather modification with 0.35 M $Na_2S_2O_5$. has an adsorption capacity of Fe(III)) 129.87 mg/g [22].

The breaking process in these bonds will have more adsorption sites [49]. This reaction is carried out through a stirring process for 10 minutes at a temperature of 65 ° C. The function of stirring is to accelerate the activation process. After that, the duck feathers are cooled by being left for 2 hours and filtered using filter paper and rinsed with distilled water until neutral. The duck feather samples obtained are then dried using an oven at a temperature of 80 ° C. This reaction process is carried out by heating and stirring so that the s ample can be mixed perfectly. Then the results of the duck feather powder modified with $Na_2S_2O_5$are entered. The mixed sample is added with maleic acid as a coupling agent [50-52]. Then the sample is molded in a hot state in order to produce a composite sample in the form of pellets. Composite samples that are already in the form of pellets must be dried so that the xylene solvent contained in the sample can evaporate. The results obtained were in the form of duck feather keratin-polyethylene (HDPE) composite adsorbents in the form of pellets as shown in Figure 2.

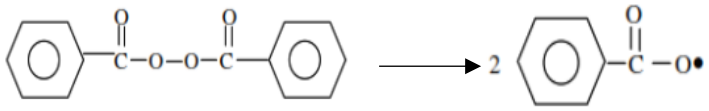
Fig. 2. Duck feather keratin- $Na_2S_2O_5$ -HDPE composite

The ratio of duck feather powder modified with $Na_2S_2O_5$ and polyethylene (HDPE) is 30:70. This ratio is the most perfect ratio for adsorption, where the pellets obtained are perfectly formed but the surface of the duck feathers is still visible so that it can still function as an adsorbent.

The application of this composite in the form of pellets has the advantage that it can be reused, thus reducing production costs [22].

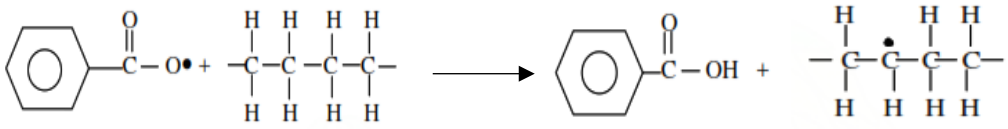
The stages of composite formation are as follows: peroxide decomposition stage, initiation stage, propagation stage, chain transfer stage and termination stage (Scheme 1).

1. Peroxide decomposition stage



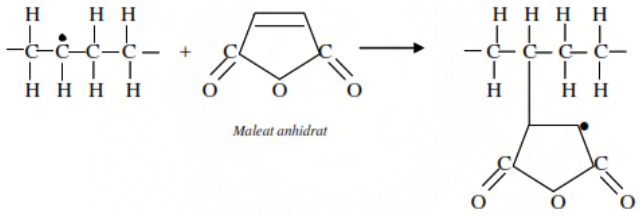
Benzoyl Peroxide benzoyloxy radicals

2. Initiation stage

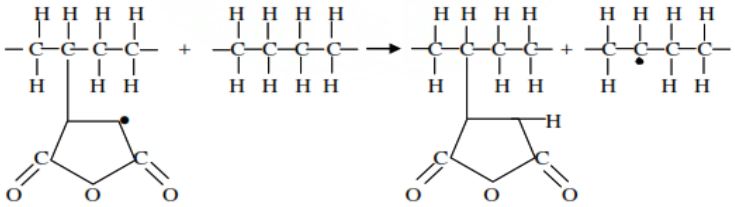


Polyethylene

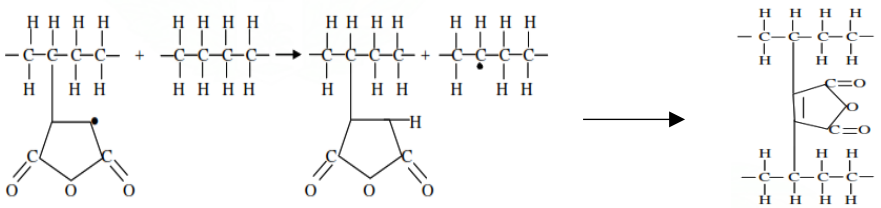
3. Propagation stage



4. Tranfer chain stage



5. Termination stage



Scheme 1. The stages of composite formation

FTIR spectrum can identify the functional groups of duck feather adsorbent, whether the adsorbent is able to adsorb manganese solution, which is indicated by changes or shifts in the groups on the duck feather adsorbent before modification, after modification with $Na_2S_2O_5$, HDPE, and after modification contacted with 100 ppm Mn solution. Identification of functional groups contained in the adsorbent is done by analyzing the spectrum results obtained. The results of the characterization of duck feather adsorbent before modification, after modification with $Na_2S_2O_5$, HDPE, and after modification contacted with 100 ppm Mn solution are presented in (Fig. 1 Supp.).

Identification of the functional groups of duck feather keratin $Na_2S_2O_5$ and duck feather keratin- $Na_2S_2O_5$ - HDPE composite can be seen in Table 1.

The FTIR spectrum can explain changes in chemical structure by detecting vibrations of chemical bonds in molecules. Bending vibrations, which are vibrations that cause changes in bond angles. While stretching vibrations, which are vibrations that cause changes in bond length. Based on (Fig. 1 Supp.), it shows the presence of an O-H groove group (alcohol) at a wave number of 3263.52 cm-1. S-H stretching vibrations (asymmetric) are also seen at a wave number of 2913.20 cm-1 which indicates an alkane group. There is amide I with a C=C conjugated C=O group at 1626.63 cm-1 and there is also amide II with an N-H group at 1552.15 cm-1. The infrared spectrum of duck feather adsorbent before modification and modified duck feathers show several typical groups such as alcohol (O-H), alkane (C-H), amide I (C=C) and amide II (N-H). The infrared spectrum of duck feather keratin composite - $Na_2S_2O_5$ -HDPE shown in the Figure shows changes, namely the shift in absorption values at certain wavelengths. The shifted absorption is the C=O group at a wave of 1632.78 cm-1 and the shift in the N-H group, at a wave of 1538.54 cm-1. The presence of changes in the absorption band pattern of the absorption peaks of functional groups such as amide I region (C=O) and amide II (N-H) is thought to have proven the interaction between duck feather adsorbent and HDPE solution. The infrared spectrum of duck feather adsorbent after modification which was contacted with 100 ppm Mn solution also showed a shift in absorption value. The shifted absorption is the C=O group at wave 1661.46 cm^{-1} amide I functional group The duck feather keratin composite $Na_2S_2O_5$ HDPE spectrum at 1626.12 cm^{-1} shows a conjugated C=O bond C=C, this comes from maleic anhydride. At 2848.47 $^{cm-1}$ shows CH_2 from the HDPE ethylene group [39]. NaOH on duck feathers in acid mine water, the spectrum results are in accordance with the keratin functional group because it shows the absorption of the CH, CO, N-H_2 groups [53]. The FTIR spectrum of duck feathers modified with NaOH shows absorption bonds at 1392.97 cm-1 and absorption at 1237.06 cm-1 of hydrogen-bonded NH groups (amide A, NH stretching), amide I (C=O stretching), amide II (flexible NH), Amide III (CN stretching), and Amide IV.

The FTIR spectrum of the keratin duck feather–$Na_2S_2O_5$–HDPE composite exhibits an absorption band at 1632,78 cm^{-1}, indicating the presence of conjugated C=C and C=O bonds, which are attributed to the maleic anhydride incorporated during the composite preparation. The absorption observed at 2913,20 cm^{-1} corresponds to the CH stretching vibration from the ethylene groups in HDPE. These findings are in agreement with previous studies on the copolymerization of LLDPE with maleic anhydride [54-57]. The reaction between Mn and keratin from duck feather can be explained, keratin Duck Feather (DF) at (isoelectric point pH ≈ 4, sorption and proton-desorption of metal cations can take place on the carboxyl pKa−COOH ≈ 4 and amino pKa-NH_3 + ≈ 10) groups. Metal complexes can be formed with the participation of water or without it with cordination numbers 4 and 6 as the most common. The formation of a cationic electroneutral metal complex with M^{2+} for keratin is possible according to two ways:

1. Deprotonation of the ammonium group (H^+ 3N∼)2DF(∼COO−)2:

$$Mn^{2+} + \{(H^+_3N\sim)2DF(\sim COO^-)_2 \leftrightarrow DF[(\sim COO)_2Mn(H_2N\sim)_2]\} + 2H^+$$

The amino group of keratin in a neutral medium can also be in the hydrated form (∼NH_2·H_2O ≈ ∼NH_3 +·OH^-). In this case, in aqueous solutions (pH 7), one can allow its participation in the sorption of metal cations with the formation of hydroxide-amine, electroneutral, cationic metal complexes on the biosorbent surface in electroneutral form [(∼NH_2)2Mn$(OH)_2$].

Table 1. Analysis of functional groups in the FTIR spectra of $Na_2S_2O_5$ duck feather keratin and duck feather keratin composite-$Na_2S_2O_5$ -HDPE

Duck feathers (cm^{-1})	Modified $Na_2S_2O_5$, (cm^{-1})	duck feather keratin-$Na_2S_2O_5$ -HDPE composite (cm^{-1})	duck feather keratin-$Na_2S_2O_5$ -HDPE composite -Mn (cm^{-1})	Numberwave (cm^{-1})	Functional group
3263,52	3263,52	3263,52	3263,52	3500-3250	O-H
2913,20	2913,20	2913,20	2913,20	2850-2920	C-H
2847,64	2847,64	2847,64	2847,64	2850-2920	S-H
1626,63	1626,63	1632,78	1661,46	1600-1680	Amide I C=C C=O
1552,15	1552,15	1538,54	1538,54	1500-1600	Amida II N-H

However, since the sorption of copper cations is accompanied by a decrease in the acidity of the aqueous phase (pH increases), thus in this case the proton, on the contrary, passes from the aqueous phase to the sorbent, therefore, such sorption way must be rejected. 2. With preservation of the salt form of the ammonium group, due to the participation in the sorption of copper cations with the anion in the salt form MX2 with the formation of the carboxylate, electroneutral, cationic complex $(XH_3N\sim)2DF$ [$(\sim COO)2Mn$].

The participation of an ions in the sorption process determines the endothermic nature of the sorption of cations. Such competitive, equilibrium, equivalent, con sistent salt sorption of copper cations, protons and anions on carboxyl groups of keratin wool in anionic form can be expressed by equations.

2. Mn^{2+} ions sorption:

$2X^- + Mn^{2+} + \{(^+H_3N\sim)2DF(\sim COO^-)_2 \leftrightarrow (XH_3N\sim)_2DF[(\sim COO)_2Mn]\}$.

Protons sorption:

$2X^- + 2H^+ + \{(^+H_3N\sim)2DF(\sim COO^-)_2 \leftrightarrow (XH_3N\sim)2DF(\sim COOH)_2\}$.

In an acidic medium, the protonation of amino groups takes place along with the filling of carboxyl groups with protons which are transferred from anionic to H-form. In accordance with competitive, equivalent, coordinated displace ment of metal cations (proton-desorption) from the anionic centers of the sorbent, sorption of M^{2+} by keratin sorbent begins to decrease with increasing acidity. As a result, competitive, equilibrium, equivalent, coordinated sorption of Mn^{2+} and $2H^+$ (proton-desorption) can be re presented by the following equation:

$Mn^{2+} + \{(XH_3N\sim)2DF(\sim COOH)_2 \leftrightarrow (XH_3N\sim)2DF[(\sim COO^-)_2Cu]\} + 2H^+$

Competitive, equivalent, equilibrium sorption of protons and metal cations takes place at the same sorption sites with the formation of electroneutral salt complexes in the ratio $M^{2+}/2H^+$.

The limiting sorption capacities of keratin and cellulose sorbents will be determined by the amount of excess acid groups on the surface of the sorbents and by their basicity. The different nature, composition and structure of the polymers and their sorption centers ($-CH_2-COOH$ and $-CHOH-COOH$) determine the temperature de pendence of sorption process with participating of keratin and cellulose [58].

α-amino acids ($R-CH(-NH_2)$ -COOH) form with heavy metal ions chelated complexes [59]. However, in the polyamides in the α-position, the carboxyl group contains the amide group: R- CO-NH-CH_2-COOH. Practically, low basic properties of carbamide nitrogen exclude its participation in chelate complexes. The protein molecule is zwitter-ionic (ampholytic) which is based on the equivalent content of acidic and basic groups in the side chains and their distribution along the chains, as generally terminal amino and carboxyl- groups, contribute slightly to the total charge of the molecule. Depending on the pH of solution, the protein molecules have positive (acidic region) or negative (in alkaline region) excess charge, and in both cases their hydration and solubility increase. Regardless of the sign of the charge, the decisive factor determining the hydration is the difference between positive and negative charges on the protein molecule.

The ratio of carboxyl and amino groups in wool keratin, -COOH /-NH_2 >1and,asaconsequence, the isoelectric point is located within pH range 3.4–4.5 [59-60].

Probable structure of the coordination site with these groups participation is: This structure (an intrachain complex in wool keratin) could be formed if two carboxyl groups of two neighboring protein chains mat ched. Taking into account the expected value of such fragments fre quency (50 per g of wool), Cu(II) uptake associated with the carboxylic residues can reach 150–300 μmoles/g of wool [61].

The reaction between Mn and keratin from duck feathers is described as Fig 3.

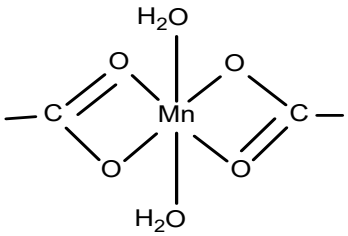


Fig. 3. Reaction Mn^{2+} and keratin

3.3. Determination of optimum volume of $Na_2S_2O_5$ modified duck feather HDPE composite in Mn solution adsorption

The determination of the optimum volume was carried out in order to determine in what volume the interaction of duck feather keratin-HDPE composite adsorbent can optimally absorb metal ions. The volume variations used in this study were 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 liters. The adsorbent used was 17.5 g and the concentration of manganese solution was 100 ppm as much as 2000 mL.

The adsorbent was separated by filtration, so that the filtrate obtained could be analyzed by atomic absorption spectrophotometer. The results of the study on the adsorption of manganese (II) metal ions after adsorption will be compared with the initial concentration to determine how much manganese metal ions were adsorbed. The metal ions adsorbed for all variations can be seen in Figure4.

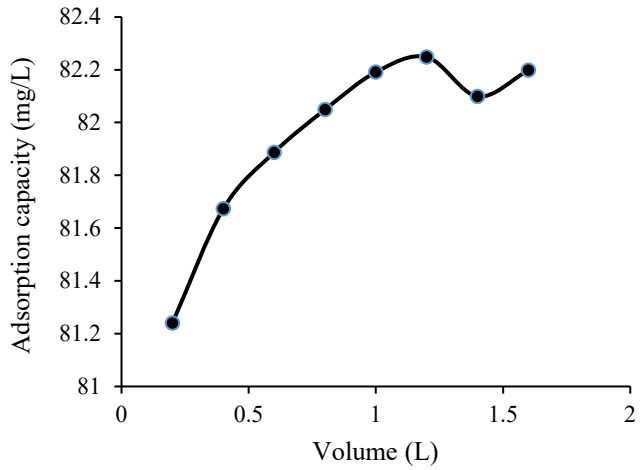


Fig. 4. Relationship between volume and adsorbed Mn^{2+} by filter

Based on the graph of the relationship between volume and adsorbed Mn, it can be seen that at a volume of 0.2 liters, the adsorption that occurs is 81.240 mg/L. This occurs because at that volume the active functional groups in the adsorbent have not reached saturation, there are still many active groups that have not been used to adsorb Mn metal ions . At a volume of 0.8 liters, the adsorption process increased by 82.049 mg/L and adsorption at a volume of 1.2 liters was 82.248 mg/L. At a volume of 1.4 liters, the adsorbent experienced a decrease in the absorption capacity. This occurs because the volume between the adsorbent and the adsorbate exceeds the best volume, so that the active group on the adsorbent is too saturated and there is a possibility of a desorption process or the release of Mn metal ions that are already bound to the active group of the adsorbent . In volume, the elimination efficiency will increase with volume because the surface area of the adsorbent is large. The adsorption process is constant after equilibrium because the surface of the adsorbent is almost completely used by metal ions, and an increase in electrostatic repulsion between the incoming metal ions and the adsorbed metal ions. If the results of this study are compared whit used duck feather keratin which reached the best condition at a volume of 2 liters. This shows that the volume of duck feather adsorbent is able to bind 2 liters of Fe solution [39].

3.4. Determination of adsorption capacity of duck feather modified $Na_2S_2O_5$ and HDPE composite in continuous Mn solution

The determination of adsorption capacity carried out in this study can reduce the concentration of Mn metal in duck feathers. In the duck feather composite modified by $Na_2S_2O_5$ and HDPE is inserted into a cylindrical tube made of glass, then 17.5 g of modified duck feathers are inserted into the cylindrical tube, foam/sponge is given below and above the cylindrical tube to hold the incoming water and to hold the duck feather adsorbent. Then at the bottom of the tube there is a tap to drain water with a concentration of Mn 100 ppm, the flow of Mn solution is measured every 60 mL/minute. The 100 ppm Mn solution is flowed at a rate of 0.2 liters/minute. The effluent solution is collected and taken periodically every 200 mL/minute, then the concentration of Mn in the effluent is measured using AAS. Effluent collection was stopped when the effluent adsorbance was saturated so that the adsorbent was unable to adsorb the Mn solution, the experiment was repeated 2 times using new modified duck feathers.

Later, the Co and Ce values will be obtained from this study. Where the initial concentration of the Mn solution is called Co (mg/L), and Ct is the effluent concentration per volume of collection (mg/L). Determination of the adsorption rate constant (Kth) is carried out to obtain a reaction kinetic constant which aims to determine the amount of adsorbate (x) that can be absorbed by each unit mass of adsorbent (M) and is expressed as qo (mg adsorbate/mg adsorbent). To determine the adsorption rate constant (Kth) and adsorption capacity (qo), a kinetic approach calculation is used as in Equation (1) and (2). The data required are influent concentration, effluent concentration, discharge, adsorbent mass and processed volume. The processed volume is obtained by multiplying the discharge by the operating time. The discharge used is 0.2 liters/minute.

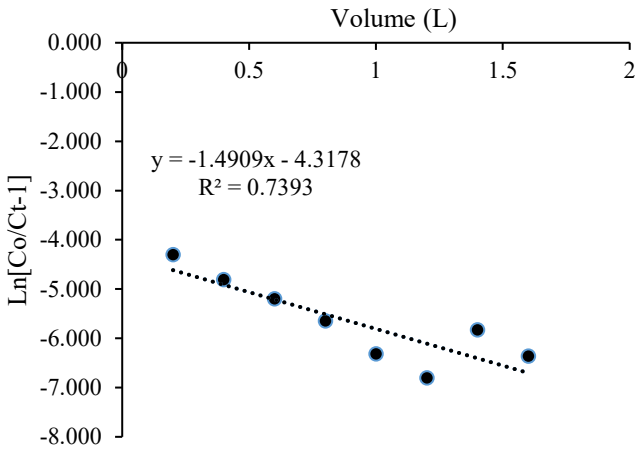


Fig. 5. Adsorption capacity using the Thomas equation

Thomas equation shows that linear equation is y = -1.4909x – 4.3178 and R^2 0.739. Kth is 49.346 mL/mg/menit. The Thomas constant data and adsorption capacity obtained from the Thomas equation with a comparison of adsorbent types. The constant values of Kth and qo can be known through the slope and intercept values of the equation shown in Figure 5. The Thomas constant obtained is inversely proportional to the adsorbance capacity of each adsorbent. This is in accordance with the Thomas equation that has been applied in this study which shows that the adsorbance

capacity is obtained inversely proportional to the resulting Thomas capacity. From the calculation of the Thomas equation above, it can also be concluded that the highest adsorbance capacity in the absorption of Mn at a weight of 17.5 g with the type of duck feathers, namely the absorption of duck feather Mn with an adsorption rate constant (Kth) of 49.346 mL / minute and for the adsorption capacity (qo) of 17.029 mg / g.

Dencity Polyethylene (LDPE) and Linear Low Density Polyethylene or linear polyethylene (LLDPE) has been widely carried out, including research on keratin fibers from chicken feathers with LDPE where keratin feather fibers can be used. directly inserted into the polymer using a thermomechanical mixing technique, and from the results of physical and microscopic properties testing showed an interaction between the fiber and the polymer without the need for a bridging agent or chemical treatment [62]. The results of research using composites with HDPE include the manufacture of date fiber composites with polyvinyl chloride (PVC)-HDPE which shows an increase in water absorption performance, morphology, thermal, mechanical, dynamic-mechanical, rheological, and water absorption [36]. The manufacture of ensete fiber composites with maleic anhydrous and HDPE showed that the addition of ensete fiber resulted in a stiffer and harder composite which caused a decrease in elongation at break. The addition of 5 wt% maletic anhydride compatibilizer to 25 wt% HDPE ensete fibers increased fiber-matrix adhesion [63]. The manufacture of bagasse fiber composites with HDPE showed that the highest tensile strength was obtained in the composition of HDPE plastic and bagasse fiber by volume of 60%: 40% with an average value of 15.5 MPa, while the highest bending strength was obtained in the composition of HDPE plastic and bagasse fiber by volume. 60% : 40% with a mean value of 16.8 MPa [38]. The results of research on filter regeneration that have been carried out include the use of KMnO4- to produce 84% iron and 96% manganese from manganese dioxide-based filter media. KCl regeneration from zeolite filter was able to remove ammonium ions up to 10.7 mg/L [64]. The use of nanomaterials that have properties of catalysis, adsorption, reactivity, larger surface area makes these materials more effective in wastewater treatment. Different types of nanomaterials are being used to remove different contaminants from wastewater. Activated carbon, carbon nanotubes, titanium oxide, magnesium oxide are some examples of nano-adsorbents used for the removal of heavy metals from wastewater [65]. Research using activated carbon from teak (Tectona grandis) and shea (Vitellaria paradoxa) charcoal can remove 92.5–100% Fe and Mn for low flows up to 1.2 m3/hour. The adsorption constant was obtained for Yoon-Nelson; 0.3095 and Adams-Bohart; 0.07335 at r squared values of 0.9728 and 0.9841, respectively, can be used to generate and predict Fe and Mn adsorption data required for the design of water treatment systems [43]. Research on the use of sludge containing iron from groundwater treatment plants and chitosan made of granular adsorbents showed that the adsorbent was able to remove As (V) from contaminated water in the filter column application, and the adsorption capacity was 20.405 mg at a flow rate of 5 mL/min, and after regeneration it still reached 19,623 mg. The Yoon-Nelson model proved to be better for describing this adsorption curve [44].

Adsorbents made of Nickel nanoparticles (NiNPs) supported on double-walled activated carbon nanotubes (MWCNTs) for Pb(II), As(V) and Cd(II) remediation have maximum adsorption capacities of 481.0, 440.9, respectively. and 415.8 mg/g were obtained for and showed a better fit in the Thomas model [45]. The adsorption of walnut shells on Cr(VI) for the bath system followed the Langmuir isotherm (KL = 0.6754 L/mg, R2 = 0.9996) and followed the equation of Yan et al in the dynamic system (KY = 5903.63 mL/(mg min) , R2 = 0.978). Regeneration of walnut shells was carried out with 0.5 M NaOH solution and the absorption capacity recovered 57.71% [42]. The adsorption of Zn^{2+} by chicken feathers in batch and continuous systems showed that the adsorption capacity was 4.31mg/g at 30ºC C and pH 5 and in the continuous system followed the Thomas model, with feed flow rates <5.0 mL/min allowing higher metal retention. effective in packed columns [66].

4. Conclusion

The infrared spectrum of duck feather adsorbent before modification and modified duck feathers show several typical groups such as alcohol (O-H), alkane (C-H), amide I (C=C) and amide II (N-H). The shifted absorption is the C=O group at a wave of 1632.78 cm-1 and the shift in the N-H group, at a wave of 1538.54 cm-1. The presence of changes in the absorption band pattern of the absorption peaks of functional groups such as amide I region (C=O) and amide II (N-H) is thought to have proven the interaction between duck feather adsorbent and HDPE solution. The infrared spectrum of duck feather adsorbent after modification which was contacted with 100 ppm Mn solution also showed a shift in absorption value. The shifted absorption is the C=O group at wave 1661.46 cm^{-1} amide I functional group The duck feather keratin composite $Na_2S_2O_5$ HDPE spectrum at 1626.12 cm^{-1} shows a conjugated C=O bond C=C, this comes from maleic anhydride.

The continuous capacity adsorption modified duck feather- $Na_2S_2O_5$-HDPE composite of Mn by Thomas equation at a weight of 17.5 g with an adsorption rate constant (Kth) of 49.346 mL / minute is 17.029 mg/g.

Supplementary files

Supplementary file 1.

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