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EXPERIMENTAL STUDY ON THE USE OF CHITOSAN-COATED ACTIVATED CARBON TO REDUCE THE CONTENT OF METAL Fe THE PRODUCED WATER

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ABSTRACT

In this paper explain about levels of iron precipitate Fe (OH) in the high produced water causing corrosive properties and affect precipitation the channel pipe. Fe bacteria also cause odor and bad taste in the water. The aim from this research is want to know how the effect of the use of activated carbon, chitosan and chitosan-coated activated carbon (CCAC) to absorb metal ions Fe in produced water. The study was conducted by the method of adsorption in batch with initial concentration in produced water Fe 27.34 ppm. 90 minutes contact time and adsorbent mass varies, 0, 3, 6, 9, 12, 15, 18, 21, 24, 27, and 30 grams. The results showed that the CCAC adsorbent mass weighing 18 grams can reduce the metal ion content of Fe in the produced water up to 93%, Chitosan with a mass of 24 grams adsorbent capable of up to 83.9% while the activated carbon is only capable of amounting to 65.3% by mass of adsorbent 30 grams. The model used is the adsorption isotherms of Langmuir and Freundlich adsorption isotherms to determine the appropriate model in the use of adsorbent CCAC. Langmuir adsorption isotherm equation linearized equation ($y = 0.4816x + 0.6294$) with $R^2 = 0.9956$ whereas the adsorption isotherms Freundlich equation ($y = 0.1347x + 0.1164$) with $R^2 = 0.9813$.

Keywords: chitosan, adsorption levels, iron, produced water, activated carbon, coated.

INTRODUCTION

Background

Produced water is water trapped in underground formations that is brought to the surface along with oil or gas during exploration and production activities. This water occurs naturally in formations where oil and gas is found, when oil and gas are produced, they are brought to the surface with produced water as a combined fluid. Physical and chemical properties of produced water vary greatly depending on the geographical location of the field, geological formation, and the type of hydrocarbon products produced. The nature and volume of produced water can even vary over the lifetime of the reservoir [1]. Contact between the water reservoir rock formations with a number of mineral components will dissolve rocks into the water and affect the quantity of each component is dissolved. The main component contained in the produced water is hydrocarbons, salts, metals, radionuclides and chemicals added during production. Produced water is also referred to as brine or water formation [2].

Subsequent studies showed that the active carbon with the shape of hollow mesoporous carbon spheres is very good as adsorbent bilirubin [3], besides the use of activated carbon from apricot seeds are able to absorb metal ions Cd^{2+}, Cr^{3+}, and Ni^{2+} respectively 33.57 mg/g, 27.21 mg/g, 24.21 mg/g [4].

Chitosan (β-1.4-2-amino-2-deoxy-D-glucose) is a natural polymer that number is very abundant after cellulose [5]. Chitosan forms aldimines and ketimines with aldehydes and ketones, respectively, at room temperature [6]. Various studies have been conducted on the use of chitosan and chitosan, including modifications to the user along with other materials to reduce the content of heavy metals in water. While other research states that Thiourea cross-linked chitosan (TCCTS) capable of absorbing metals Fe (II) and Fe (III) through synthesis with pH = 5 and adsorption equilibrium time is 60 minutes [7]. In other studies indicate that oil palm shell charcoal coated with chitosan can lower 86% Cr with adsorption methods of batch [8]. Objectivity of this research is to know how to influence the use of activated carbon to absorb the chitosan-coated metal Fe in produced water where the results of the initial analysis of Fe content in produced water in one field of oil and gas production amounted to 27.34 mg/l and is potentially causing corrosion and scaling of piping ends is disturbing productivity.

The aim of the research

The purpose of this study is a follows
a) Knowing the morphology of chitosan-coated activated carbon (CCAC).
b) Determining the dosage of activated carbon adsorbent, chitosan and chitosan-coated activated carbon optimum needed to lower metal content of Fe / liter produced water.
c) Adsorption isotherm models to determine the appropriate model in the use of adsorbent CCAC.

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THEORY

Langmuir adsorption isotherm based on the assumption that the adsorbent has a homogenous surface and can only adsorb one molecule for every molecule adsorbent, there is no interaction between the molecules absorbed, all the adsorption process carried out by the same mechanism, only formed a single layer while the maximum adsorption. Langmuir adsorption isotherm model equation can be written as follows:

$$q_e = \frac{Q_o\, K_L\, C_e}{1 + K_L\, C_e} \tag{1}$$

where q_e the amount of metal ion is absorbed by the adsorbent (mg/g), C_e concentration at equilibrium conditions (mg/l), Q_o The maximum absorption capacity to form a single layer (mg/g), dan K_L Langmuir equilibrium constant (l/mg). K_L and Q_o the characteristics of Langmuir adsorption isotherm equation and can be determined from the linearized Langmuir adsorption isotherm equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L\, Q_o} + \frac{C_e}{Q_o} \tag{2}$$

Plot C_e/q_e vs C_e will form a straight line with an intercept $1/K_L\, Q_o$ dan slope $1/Q_o$ [9].

The essential characteristics of Langmuir adsorption isotherm model equations can also be explained in the form of dimensionless constant separation factor (R_L) are written as follows:

$$R_L = \frac{1}{1 + K_L\, C_o} \tag{3}$$

Where is the equilibrium constant of the Langmuir K_L (l/mg) and C_o is the initial concentration of the solution (mg/l). R_L value indicating whether irreversible adsorption ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavourable ($R_L > 0$) [8].

Freundlich adsorption isotherm models based on the assumption that the adsorbent having a heterogeneous surface and each molecule has the potential absorption different. The equation of adsorption isotherm models is an empirical equation is generally written as follows:

$$q_e = K_f\, C_e^{\frac{1}{n}} \tag{4}$$

wherein an amount of metal ions q_e absorbed by the adsorbent (mg/g), C_e concentration at equilibrium conditions (mg/l), K_f Freundlich isotherm constants showing the adsorption capacity (mg/g), and n the intensity of adsorption. K_f and n value can be determined through the linearized Freundlich adsorption isotherm equation is written as follows:

$$\log q_e = \log K_f + \frac{1}{n}\, \log C_e \tag{5}$$

plot $\log q_e$ vs $\log C_e$ will form a straight line with an intercept $\log K_f$ and slope $1/n$ [9].

RESEARCH METHODOLOGY

Produced water to be used in this study came from one of the field of oil and gas production in Indonesia, with a concentration of 27.34 ppm Fe and pH 6.0. Chitosan is commercially used technical grade. Activated carbon used is a commercial activated carbon. The optimum contacts time of 90 minutes.

The adsorbent used is activated carbon, chitosan, chitosan-coated activated carbon (CCAC) at a dose of adsorbent: 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 g/l produced water.

Chemicals 2% H_2SO_4, $CaCO_3$ 2%, 0.5% NaOH solution is used as activated carbon for the activation process. Glacial acetic acid used to make chitosan gel, as well as iron reagent as a reagent verrover on HACH DR 2800 Spectrophotometer.

The adsorbent CCAC

The process of making adsorbent Activated-Carbon Coated Chitosan consists of two stages: the manufacture of chitosan gel and chitosan gel coating on the surface of activated carbon. Manufacture Chitosan, chitosan gel is dissolved in 1% acetic acid, is heated at a temperature of 40-45 °C for several minutes with constant stirring. The solution was then cooled to room temperature to form a gel.

Chitosan coating process on the surface of activated carbon is done by soaking 100 g of activated carbon in 100 ml chitosan gel is then heated at a temperature of 40-50 °C for 1 hour, stirring frequently. Activated carbon that is been coated with chitosan and then dried at room temperature for ± 3 days. During the immersion of chitosan gel will coat the surface of activated carbon and form a layer [8].

RESULTS AND DISCUSSIONS

SEM analysis

In this study CCAC samples were analyzed by using SEM to determine the structure of the activated carbon surface after being coated with chitosan. Here is a picture of the topography of the surface of chitosan-coated activated carbon.
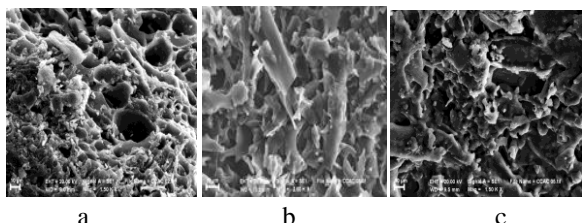
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Figure-1. Chitosan-coated surface of activated carbon 1
(a), Surface chitosan-coated activated carbon 2 (b),
Surface chitosan-coated activated carbon 3 (c).

Figure-1 shows that the chitosan coating process on the surface of activated carbon is uneven. Figure-1(a) shows that the activated carbon surface portion not coated with chitosan. Some chitosan particles visible on the surface of active carbon showed that chitosan is not dissolved perfectly during the manufacturing process so that there are several chitosan gel particles still left in the chitosan gel and cause the coating to be imperfect. That is what causes chitosan coated on the surface of activated carbon only about ± 8%.

Figures 1(b) and 1(c) shows the most carbon activated carbon, chitosan coated perfectly on its surface. Chitosan forming a rigid matrix layer to the surface of activated carbon adsorbent surface and extend to absorption. Unequal distribution of chitosan coating on the surface of activated carbon is most likely due to the mixing process during manufacture of chitosan gel and chitosan gel coating on the surface of activated carbon is less evenly distributed, so there is some active carbon coated with a perfect and some will not. Better coating technique should be able to provide the result of chitosan coating on the surface of activated carbon is more evenly.

The timing of the achievement of equilibrium

This process is done by adding the adsorbent with a fixed dose in a 1 liter sample solution with Fe concentrations were also fixed and varying the length of contact time. The resulting filtrate was analyzed by HACH DR 2800 spectrophotometer initial Fe concentration in the sample solution at 27.34 mg/l and adsorbent dosage CCAC, chitosan, and activated carbon each 30 grams. The contact time varied from: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 minutes.

Decline in ferrous metal content in produced water is expressed in% removal where the concentration of iron is absorbed compared with the initial concentration through the following equation:

$$\% \ Removal = \left(\frac{c_0 - c_1}{c_0}\right) x \ 100\% \qquad (6)$$

where C_0 = initial concentration of Fe (mg/l) and C_1 = Concentration final Fe (mg/l) [8]. Results of analysis of the filtrate showed that the equilibrium time between each adsorbent with a metal Fe in produced water are different

from each other. The relationship between the contact time and the percentage reduction in the metal content of Fe can be seen in the graph below.
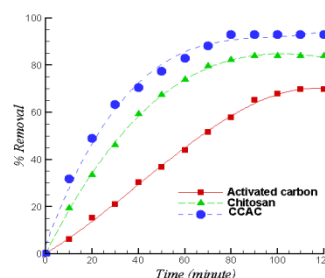

Figure-2. Effect of contact time (minutes) to decrease the metal content of Fe (% removal) in produced water for each adsorbent.

Figure-2 shows that the above can be seen that the CCAC reach equilibrium with the metal Fe within 80 minutes where the CCAC is able to reduce the content of Fe in the produced water by 93%. The equilibrium between the chitosan and the metals Fe reached at minute 90 where the metal Fe can be absorbed by chitosan up to 83.9%. On activated carbon with a metal Fe new equilibrium occurs within 110 minutes with a decrease in metal content of Fe in produced water by 69.9%.

The contact time is one of the factors that affect the adsorption process. Figure-2 shows that the percentage reduction in Fe metal in produced water increases with increasing length of contact time before finally reached equilibrium, wherein the adsorbent becomes saturated and no longer able to absorb the metal Fe. CCAC has a shorter time to reach equilibrium with the metal Fe compared to chitosan and activated carbon. CCAC also able to reduce the content of Fe metal most large when compared with two other adsorbent. The combination of active functional groups on chitosan as well as the surface area of activated carbon is able to accelerate the process of bonding metals Fe metals in produced water. This result is particularly important given the short time to reach equilibrium is an important parameter in wastewater treatment economical.

The effect of increasing doses of activated carbon adsorbent, chitosan, and CCAC to the uptake of metal ions Fe in Produced Water

This process aims to determine how to decrease the influence of adsorbent dosage Fe metal content in produced water using several different types of adsorbents. In this process adsorbent with varied doses in 1 liter added to the sample solution with Fe concentrations were also fixed for a certain time interval. The resulting filtrate was analyzed by HACH DR 2800 spectrophotometer contact time is determined based on the timing of the achievement of equilibrium between each adsorbent with Fe in produced water that is 90 minutes, which in this time

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interval chitosan and CCAC has reached equilibrium with Fe. Initial Fe concentration in the sample solution at 27.34 mg/l and adsorbent dosage CCAC, chitosan, and activated carbon was varied each: 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 grams. Analysis of the filtrate showed that the CCAC is able to reduce the content of Fe in produced water from 27.34 ppm to 1.9 ppm, or about 93% at a dose of 18 grams adsorbent. Chitosan is able to lower the metal content of 83.9% Fe at a dose of 24 grams, while the activated carbon can only reduce the metal content of 65.3% Fe at a dose of 30 grams. The relationship between dose and the addition of metallic Fe percentage reduction in produced water can be seen on the curve below.
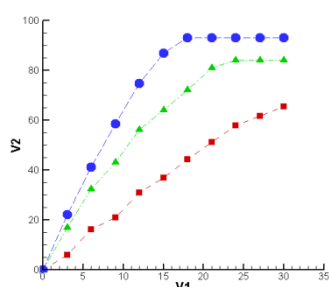

Figure-3. Effect of increasing dosage of activated carbon adsorbent, chitosan, and the CCAC to the absorption of the metal ion Fe in produced water.

From Figure-3 it can be seen that the percentage reduction in Fe metal increases with increasing doses of adsorbent. This condition can be understood that with the greater number of adsorbent used, the greater the ability to perform adsorption. CCAC is able to reduce the content of Fe metal with the greatest adsorbent use the smallest dose is 18 grams at equilibrium conditions, this result is smaller than the dose used during the time of the determination of equilibrium in which the doses used at the time was 30 grams. The same condition also occurs chitosan which only takes adsorbent dosage of 24 grams to reduce the content of Fe to the achievement of equilibrium conditions. On activated carbon, adsorbent required larger doses to achieve equilibrium within 90 minutes given a dose of 30 grams of activated carbon can only be reached equilibrium within 110 minutes.

Differences in the amount of adsorbent dosage is added until there is equilibrium between each adsorbent and metal Fe in produced water indicates that the adsorbent surface modification turns giving better results. The combination of active functional groups on chitosan as well as the surface area of activated carbon is able to bind metal metallic Fe in an amount greater than the use of separately. Terlapiskan number of chitosan on the surface of activated carbon is possible also affects the effectiveness of metal absorption Fe, where to thicken the layer of chitosan on the surface of activated carbon can improve the lot of metallic Fe is absorbed. Besides,

chitosan is also likely to bind to other metals in produced water because the amine group in chitosan are very reactive and easy to interact with the anion and the other negatively charged metal ions so that the absorption of the metal Fe to be imperfect.

Adsorption isotherms

The relationship between substances that are absorbed by the adsorbent and the concentration of the solution at equilibrium conditions can be known through the adsorption isotherm. This study uses a model of Langmuir and Freundlich adsorption isotherm. Linerisasi Langmuir and Freundlich isotherm equation used to determine the suitability of the results of a study of the adsorption isotherm model of Langmuir and Freundlich. Langmuir adsorption isotherm model test is done by making the curve relationship between C_e/q_e against C_e. Langmuir adsorption isotherm model of the curve can be seen in the picture below:
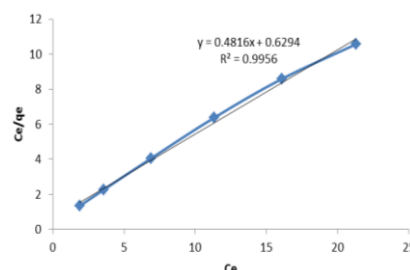

Figure-4. Curve relationship between C_e/q_e against C_e

Plot C_e/q_e vs C_e will form a straight line with y-intercept $1/K_L Q_o$ dan slope $1/Q_o$ [9]. From Figure-6 it is known that the Langmuir adsorption isotherm is means that the maximum absorption capacity of the metal ion Fe CCAC in produced water for 2.076412 mg/g CCAC. Value R_L is 0.045621 which means that the favorable adsorption equilibrium, in addition to the value of R^2 = 0.9956 indicates that the data results of the study in accordance with the model of Langmuir adsorption isotherm models.

Freundlich adsorption isotherm model test is done by making the curve of the relationship between log q_e against log C_e. Freundlich adsorption isotherm model of the curve can be seen in the picture below:
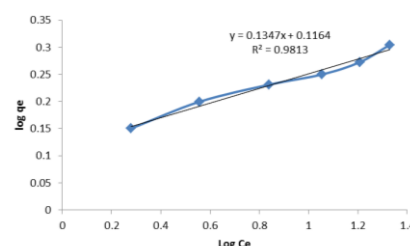

Figure-5. Curve relationship between $log\ q_e$ to $log\ C_e$.

10509

plot $log\ q_e$ vs $log\ C_e$ will form a straight line with an intercept $log\ K_f$ and slope $1/n$ [9]. From Figure-5 it is known that Freundlich adsorption isotherm model is means that the absorption capacity of the metal ion Fe CCAC in produced water for 1.30737 mg/g CCAC. Value of $R^2 = 0.9813$ indicates that the data results of the study in accordance with the model Freundlich adsorption isotherm models.

By comparing the value of R^2 on the model of Langmuir and Freundlich adsorption isotherm, it is known that the data of this study is more fitting to the Langmuir adsorption isotherm models. This suggests that the adsorption of metal ions on the surface of the CCAC Fe occurs only in one layer (monolayer). Some previous studies also showed results similar where the adsorption of metal ions of Cr on the surface of charcoal palm coated with chitosan [8], adsorption of Pb^{2+} on bark powder peanut, adsorption of metal ions Zn^{2+} on rice husk [9] more inclined to the model isotherm Langmuir adsorption.

CONCLUSIONS

From the results of experiments and calculations, it can be concluded:

a) From SEM analysis CCAC coated on the surface of activated carbon is only about ± 8%.
b) The optimum adsorbent dose required to reduce the metal content in produced water Fe is 18 grams for CCAC, 24 grams to 30 grams of chitosan and activated carbon.
c) The optimum adsorbent dose required to reduce the metal content in produced water Fe is 18 grams for CCAC, 24 grams to 30 grams of chitosan and activated carbon (y = 0.4816x + 0.6294) with $R^2 = 0.9956$ while the Freundlich adsorption isotherm equation (y = 0.1347x + 0.1164) with $R^2 = 0.9813$.

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