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To cite this article: ZU Halim et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 536 012007

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Removal and Kinetics Adsorption Fe (II) Ions in Ground Water using Sugarcane Bagasse of Various Treatments Adsorbent with Column Method

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Abstract. After the water adsorption process, the content of Fe (II) ion meets drinking water standard below 0.3 ppm. Based on the kinetic indicator of the absorption coefficient of correlation ($R^2$), the adsorption rate constant $k_1$ and $k_2$ and the calculated $q_e$ and $q_e$ extrapolation data can be concluded the content of Fe (II) ions in groundwater above 0.3 ppm can cause serious problems for human health. A relatively effective, efficient, safe, environmentally friendly separation method is the adsorption method. The mechanism of adsorption of Fe (II) ions in the well water can be studied using pseudo-first-order and pseudo-second-order. Based on the experimental design, fixed variables consisted of 50 g of adsorbent, 20 mesh particle size, 10-liter adsorbate volume, 4 liters/min flow rate and operating temperature at room temperature. The independent variable consists of contact time and the type of treatment of the adsorbent. Variation of contact time 0; 30; 60; 90; 120; 180; 240 minutes and type of adsorbent treatment: without treatment, physical treatment and chemical treatment ($H_2SO_4$ 0.5N and NaOH 0.5N). The results showed that the adsorption of Fe (II) ion was influenced by contact time and type of adsorbent treatment. That the kinetic adsorption of Fe (II) ion is showing the second order pseudo adsorption kinetics with $R^2$ value for the adsorbent without treatment: 9636, physical treatment: 0.9028, treatment with $H_2SO_4$ 0.5N: 0.9578, treatment with NaOH 0.5N: 0.9967. Results of $q_e$ of adsorption kinetics for non-treated adsorbents: 0.224 mg/g, physical treatment: 0.257 mg/g, treatment with $H_2SO_4$ 0.5N: 0.258 mg/g and NaOH treatment 0.5N: 0.218 mg/g.

1. Another section of your paper

Groundwater contains a variety of metallic minerals such as Mn, Fe and Ca minerals, Mg in the form of temporary hardness and permanent hardness. Under certain conditions, the groundwater also contains dissolved gases such as aggressive CO₂, CH₄, and H₂S. Water for drinking water consumption requires Fe content of less than 0.5 ppm. There are many methods for separation of metals in water among others, treatment options recently considered for the removal of emerging contaminants from drinking water as well as wastewater are adsorption, Advanced Oxidation Processes (AOPs), Nano-filtration (NF), and Reverse Osmosis (RO) membranes [1]. Other literary sources of separation of metal components in wastewater such as iron can be carried out by various separation methods such as precipitation method, ion exchanger, adsorption and ultrafiltration [2]. The process of water purification and metal ion...
Separation by adsorption method is more widely used because it is more effective, efficient and economical [3]. Adsorption can be effective for the removal of emerging compounds; these processes can lead to the formation of oxidation intermediates that are mostly not known at this point. Conversely, adsorption processes do not add undesirable by-products and have been found to be superior to other techniques used for water treatment in terms of simplicity of design and operation, and insensitivity of toxic substances.

Components of chemical compounds that play a role in the adsorption process between metal and adsorbent are the presence of hydroxyl active groups (–OH), carbonyl (C=O), carboxyl (-COOH), amines (-NH₂), amide(-CONH₂) and thiols (-SH). Factors that may affect the Fe²⁺ adsorption process include contact time, flow rate, the particle size of the adsorbent, the temperature, type, and characteristics of adsorbate [4]. The research aims to study the decrease of Fe (II) content from groundwater and to study the phenomenon of adsorption kinetics using adsorption kinetics model of pseudo-first-order and pseudo-second-order. In addition, the metal ion adsorption kinetics can be studied through various adsorption theories such as Frequency adsorption isotherm, Langmuir adsorption isotherm and other methods. Adsorption kinetics of pseudo-first order, also known as chemisorption’s that study the phenomenon of the adsorption rate [5].

The adsorption kinetics phenomenon which takes place in the column system with the free variable of contact time with a certain flow rate can be studied according to the adsorption kinetics as pseudo-first order and pseudo-second order. The adsorption parameters are guided by the adsorption capacity at the time of contact (q), the equilibrium adsorption capacity (qₑ), correlation coefficient (R²), the adsorption rate constant k₁ and k₂. This parameter is based on initial concentration (C₀) with contact time (t₀), the concentration at time t (Cₜ), concentration on equilibrium (Cₑ).

1.1. Absorption capacity

The separation of the metal content contained in water by the adsorption method, the adsorption capacity during the adsorption process can be calculated according to the following formula:

\[ qₜ = \left( \frac{C₀ - Cₜ}{m} \right) xV \]  

(C₀: the initial concentration of adsorbate (mg/L), Cₜ: the concentration of adsorbate (mg/L) at time t (min), m: the adsorbent mass (g), Volume (V) of adsorbate(L), q: adsorption capacity (mg/g) at time t (min). The value of the adsorption capacity at equilibrium (qₑ) determined by plotting q versus t, or by the following equation:

\[ qₑ = \left( \frac{Cₑ}{m} \right) xV \]  

(Cₑ: is the concentration of adsorbate (mg/L) which is absorbed at equilibrium time, m: the mass of adsorbent (g), V: volume of adsorbate (L), qₑ: adsorption capacity (mg/g) equilibrium whose value has remained independent of time t (min). Based on the results of data processing, the qₑ value can be obtained from the graph and equations of Pseudo-first order and pseudo-second-order.

1.2. Kinetic adsorption

The behaviour or mechanism of adsorption of various types of adsorbents can be studied from the following fundamental chemisorption equations:

1.2.1. The pseudo-first order kinetics model

Pseudo-first order kinetic equations [5] expressed as in the following equation:

\[ \frac{d qₑ}{d τ} = k₁(qₑ - qₜ) \]  

(3)
Integration on conditions $q_t = 0$ s/d $q_t = q_t$ and $t = 0$ s/d $t = t$ from the above equation we get the following form of linear equation:

$$
\ln (q_e - q_t) = \ln q_e - k_1 t
$$

(4)

Parameter $q_e$ (mg/g) and $k_1$ (min$^{-1}$) can be calculated from plotting $\ln (q_e - q_t)$ versus $t$.

1.2.2. The pseudo-second-order kinetics model

The pseudo-first order can be developed into the pseudo-second order equation [6]:

$$
\frac{d q_t}{d t} = k_2 (q_e - q_t)^2
$$

(5)

Integration conditions $q_t = 0$ s/d $q_t = q_t$ and $t = 0$ s/d $t = t$ obtained the form of linear equation:

$$
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
$$

(6)

Parameter $q_e$ (mg/g) and $k_2$ (g/mg.min) can be calculated from the plot $t/q_t$ versus $t$.

2. Materials and Methods

2.1. Materials

Equipment in this study consisted of a tool for size reduction, dryer oven, analytical balance, 1000 ml glass, steamer, and demineralization unit. Chemical materials HCl 0.5N N, H$_2$SO$_4$ 0.5N, NaOH 0.5N.

Adsorbate derived from groundwater contain Fe, Mn, Ca, Mg, Cu, Zn. The adsorbents were made from bagasse with a size of -10 mesh / (+20 mesh), passed on a 10-mesh sieve and held 20 mesh.

Physical treatment using steam for 2 hours and chemically treated using NaOH 0.5N and H$_2$SO$_4$ 0.5N each for 24 hours. The adsorbents were 50 gr for each without treatment, physical treatment, treatment with H$_2$SO$_4$ 0.5N and treatment with NaOH 0.5N. Before use, each of the adsorbents is dried by the oven at a temperature of 60 $^\circ$C to 105 $^\circ$C until the constant weight.

2.2. Methods

Adsorption occurs in single columns with a diameter of 6.35 cm and a blank column height of 38 cm. Each adsorbent was inserted into an adsorption column of 50 g of adsorbent (without treatment, physical treatment, chemical treatment). Experimental design with fixed variables consisted of particle size (-10 mesh/+20 mesh), flow rate: 4 liters/minute, adsorbate volume: 10 liters, operating temperature: 30$^\circ$C. Contact time as independent variable: 0; 30; 60; 90; 120; 150; 180; 210 and 240 min, respectively.

The dependent variable is the concentration of Fe (II) ion in adsorbate (ppm).

The determination of Fe (II) concentration in the sample was analysed using Atomic Absorption Spectrophotometer (AAS) based on Fe cathode lamp with a certain length and data analysis result was done by data processing and discussion.

3. Results and Discussions

The adsorption process may employ column methods such as decreasing arsenic levels in wastewater using modified zeolites with Pb, Fe, and Ag [7]. The adsorption method, when compared to the adsorption process with the batch system (batch) with the column system, the column system is considered more applicable [8]. The fundamental difference lies in the size of the adsorbent particles used. In the particle size vessel system, we can use a much larger mesh size than using a column system. The weakness of the vessel system in its implementation is much more complicated than the column.
method. The weakness of the column system of small mesh adsorbent particle size. The factors influencing the separation of Fe (II) ions with the adsorbent of bagasse in the solution depend on pH, contact time, adsorbent dose and initial concentration of adsorbate [9].

3.1. Concentration (Ct) Fe at time t (min)

Changes in the concentration of Fe (II) ions in Table 1 to the contact time showed a significant decrease in Fe (II) concentration. In non-treated adsorbent, the decrease of Fe (II) level is not uniform. This is due to the pores of the adsorbent that are not uniform or still covered by impurities. Adsorbents treated (physical and chemical) also occur differently from one another where the adsorbent treated with the solution H$_2$SO$_4$ 0,5N its absorbency is better than those with physical treatment and with NaOH 0,5N. This is because the treatment with H$_2$SO$_4$ gives a bigger effect because H$_2$SO$_4$ is more hygroscopic than NaOH, so the pores of the adsorbent become open and not closed again by the material that covers the pores. The separation of Fe (II) ions is below the threshold 0,3 ppm Fe [10].

| Contact Time (min) | Types of Sugar Cane Bagasse Adsorbent Treatment |
|-------------------|-----------------------------------------------|
|                   | Untreated | Physical | H$_2$SO$_4$ | NaOH      |
| 0                 | 1.1900    | 1.1900   | 1.1900      | 1.1900    |
| 30                | 0.0561    | 0.8500   | 0.5600      | 0.1684    |
| 60                | 0.3931    | 0.5400   | 0.4200      | 0.1375    |
| 90                | 0.3328    | 0.0609   | 0.2700      | 0.2661    |
| 120               | 0.0984    | 0.0577   | 0.2100      | 0.1440    |
| 150               | 0.3621    | 0.0333   | 0.1016      | 0.1277    |
| 180               | 0.1244    | 0.0495   | 0.0919      | 0.1163    |
| 210               | 0.1033    | 0.0786   | 0.0951      | 0.1163    |
| 240               | 0.1863    | 0.1440   | 0.0202      | 0.1114    |

Source: Results of Analysis by SSA (2018)

3.2. Adsorption Capacity (mg/g) at time t

| Contact Time (min) | Types of Sugar Cane Bagasse Adsorbent Treatment |
|-------------------|-----------------------------------------------|
|                   | Untreated | Physical | H$_2$SO$_4$ | NaOH      |
| 0                 | 0.000     | 0.000    | 0.000       | 0.000     |
| 30                | 0.227     | 0.068    | 0.126       | 0.204     |
| 60                | 0.159     | 0.130    | 0.154       | 0.211     |
| 90                | 0.171     | 0.226    | 0.184       | 0.185     |
| 120               | 0.218     | 0.226    | 0.196       | 0.209     |
| 150               | 0.166     | 0.231    | 0.218       | 0.212     |
| 180               | 0.213     | 0.228    | 0.220       | 0.215     |
| 210               | 0.217     | 0.222    | 0.219       | 0.215     |
| 240               | 0.209     | 0.209    | 0.234       | 0.216     |

Source: Data Processing Results (2018)
Based on the data in Table 2 and Figure 1 that the adsorption capacity of Fe (II) metal absorbed into the adsorbent shows that the longer the contact time, the adsorption capacity leads to equilibrium. Equilibrium adsorption capacity ($q_e$) based on trial data and calculation data shows that the contact time to produce equivalent adsorption capacity ($q_e$) occurs between 150 minutes and 210 minutes has been reached.

### 3.3. Kinetics Adsorption

#### Table 3. Parameters of Fe (II) of pseudo-first order

| Parameter                  | Types of Sugar Cane Bagasse Adsorbent Treatment | Untreated | Physical | H$_2$SO$_4$ 0.5N | NaOH 0.5N |
|----------------------------|-----------------------------------------------|-----------|----------|------------------|-----------|
| $R^2$                      |                                               |           |          |                  |           |
| $k_1$ (min$^{-1}$)         |                                               | 0.0002    | 0.2986   | 0.7123           | 0.8036    |
| The value of $q_e$ count   |                                               | 0.227     | 0.228    | 0.234            | 0.216     |
| Extrapolated $q_e$ value   |                                               | 0.01635   | 0.0843   | 0.3506           | 0.0851    |
| Different value of $q_e$   |                                               | 0.21065   | 0.1437   | 0.1166           | 0.1309    |
| Different $q_e$ (%)        |                                               | 92.80     | 63.03    | 49.83            | 60.60     |

**Source:** Data Processing Results (2018)

In Table 3 the parameter or indicator of adsorption kinetics is the value of open coefficient ($R^2$) through the first order pseudo adsorption kinetics model. The results obtained were not significant for the unobserved adsorbent, physic perliskusn, while for chemical treatment gave relatively good results that value close to 1. However, the overall value of $R^2$ is very small from the number 1. Another parameter indicator is the reaction rate constant ($k_1$) showing very small results with a value below 5. The value of equivalent adsorption capacity ($q_e$), if compared between the $q_e$ calculated data with the $q_e$ data of extrapolation there is a very significant value difference for the adsorbent without treatment,
physical treatment, treatment with H₂SO₄ and NaOH. The difference of data respectively from the biggest to the smallest is the adsorbent without treatment: 92.80%; Physical treatment: 63.03%; treatment with 0.05N NaOH: 60.60% and treatment with H₂SO₄ 0.05N: 49.83%.

| Parameter | Types of Sugar Cane Bagasse Adsorbent Treatment |
|-----------|-------------------------------------------------|
|           | Untreated | Physical | H₂SO₄ 0.5N | NaOH 0.5N |
| R²        | 0.9636    | 0.9028   | 0.9578     | 0.9967     |
| k₂ (g/mg.min) | 8,760.3 | 64,326.6 | 23,510.4 | 1,614.4 |
| The value of q_e count | 0.227 | 0.228 | 0.234 | 0.216 |
| Extrapolated q_e value | 0.224 | 0.257 | 0.258 | 0.218 |
| Different value of q_e | 0.003 | 0.029 | 0.024 | 0.002 |
| Different q_e (%) | 1.32 | 12.72 | 10.26 | 0.93 |

**Source:** Data Processing Results (2018)

In Table 4 the value of the correlation coefficient (R²) of the second order pseudo adsorption kinetics modelling value above 0.9 is almost close to 1. When compared to the order 1 and 2 order kinetics model, the one that gives the largest R² value closest to the coefficient value of 1 is the adsorption kinetics model of pseudo-second order. R² value for adsorbent without treatment 0.9636, physical treatment 0.9028, treatment with H₂SO₄ 0.9578 and treatment with NaOH 0.9967.

The other parameters are the value of q_e count and q_e extrapolate. The ratio of this q_e to the kinetic model of pseudo-second-order, the results obtained show relatively the same value as each other. The difference is very small. For untreated adsorbents: 1.32%; Physical treatment: 12.72%; treatment with H₂SO₄ 0.5N: 10.26% and treatment with NaOH 0.5N: 9.3%. Value of q_e extrapolation of second order pseudo kinetics model for adsorbent without treatment: 0.224 mg/g, physical treatment: 0.257 mg/g, treatment with H₂SO₄: 0.258 mg/g and treatment with NaOH 0.218 mg/g. The q_e value of extrapolated one-order kinetics of q_e values generated below the calculated value by this is not true. Judging from the adsorption rate constant of the small k₁ value of the k₂ value, the effect of k₂ on the adsorption rate is greater than that of k₁. For the second-order pseudo adsorption kinetics the k₂ value for bio-adsorbent without treatment: 8,760.3 g/mg.min, physical treatment: 64,326.6 g/mg.min, treatment with H₂SO₄ 0.5N: 23,510.4 g/mg.min and activation with NaOH 0.5N: 1,614.4 g/mg.min.

Previous research on adsorption of Fe (II) uses activated carbon adsorbents from Nigerian bamboo [11], adsorption of Fe (II) ions using activated bentonite [12], adsorption Mn (II) using adsorbent of sugarcane bagasse [13] shows the adsorption kinetics taking place in accordance with the pseudo-order two kinetic model. Adsorption of Fe (II) ions using adsorbents from chitinous model chitosan meet pseudo-first-order and pseudo-second-order [14]. Adsorption of Fe (II) using chitosan meet pseudo-first-order and pseudo-second-order [15]. The experimental results showed that adsorption Fe(II) is both time consuming influenced and adsorbent.

Factors affecting the adsorption process consist of several factors, including surface area, adsorbent size, adsorbent properties, the solubility of adsorbate, shape, and size of adsorbate, temperature and acidity [16]. Comparison with the adsorption process of Fe (II) by batch method using banana stem adsorbent of water quality standard produced has not fulfilled drinking water quality standard [17]. When compared to this study with research [18] using a similar adsorbent, Fe (II) ion content after adsorption with the adsorbent of bagasse still contains Fe (II) ions of 0.128 mg/L. Thus, the results obtained by Fe (II) content remaining under the above data are between 0.0202 s/d 0.1114 mg/L or smaller than 0.128 mg/L.

4. Conclusion

Based on the data of research data processing and discussion can be concluded as follows, the removal of Fe (II) ions content in well water using adsorbent from bagasse can meet the minimum
standard of Fe (II) ions in drinking water. Moreover, the equilibrium adsorption capacity \( (q_e) \) adsorbent without treatment:0.224 mg/g, physical treatment:0.257 mg/g, treatment by H\(_2\)SO\(_4\)0.5N: 0.258mg/g and treatment by NaOH 0.5N: 0.218 mg/g. last but not least, the adsorption kinetics model of Fe(II) ions takes place following the pseudo-second-order for respectively adsorbent (without treatment, physical treatment, treatment by H\(_2\)SO\(_4\)0.5N and treatment by NaOH 0.5N).

5. Acknowledgment

Thanks to Kemenristek-Dikti who has funded this research activity based on 2018 research budget.

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