ACTIVATED ADSORBENT PREPARED FROM BOVINE BONE WASTE: PHYSICO-CHEMICAL CHARACTERISTICS, ISOOTHERM AND THERMODYNAMICS ADSORPTION OF CHROMIUM IONS IN WASTEWATER

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Abstract:
The adsorption characteristics of chromium ions in chrome electroplating wastewater on a low cost adsorbent have been conducted. Adsorbent was prepared from bovine bone waste of NaOH activated at various concentrations (0.2 to 0.8 M). Its adsorption such as adsorption isotherms and adsorption thermodynamics as well as adsorbent physico-chemical characteristics (surface active sites, crystallinity and crystal size, surface morphology and elementals composition). The result showed that amount of adsorbent surface-active sites increased because of NaOH activated, the highest at 0.4 M NaOH concentration (AT0.4 adsorbent). X-ray diffraction patterns of the adsorbents showed a wide peaks and crystal size as nanocrystalline. The surface morphology was stack of agglomerates and leached of Ca and Mg due to increase Na. The adsorption result of adsorbents to chromium ions showed that the highest adsorption ability on AT0.4 adsorbent. It was suitable for Freundlich adsorption isotherm model as physical adsorption and endothermic but the tendency to be spontaneous process.

Keywords: NaOH Activated Low Cost Adsorbent; Chromium Ions; Chrome Electroplating Wastewater; Adsorption Isotherm; Adsorption Thermodynamics.

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1. Introduction

The heavy metal ions like chromium ions (Cr) from industrial wastewater especially home industry as chrome electroplating need attention seriously before are sent to water. The chromium ions in the water exists mainly in trivalent [Cr (III)] and hexavalent [Cr (VI)] forms, entering human body by digestions. Chemical handling of Cr (VI) ion is more difficult than Cr (III) ion [1, 2]. Suksabye et al. [2] found that the electroplating wastewater is dominated by Cr (VI) ions. Its toxic effect can liver damage, elements composition, kidney, skin, disturbing enzyme activity and causes cancer. Cr(VI) is highly toxic than Cr(III). Besides, Cr(VI) has high mobility and solubility compared to Cr(III) [1, 3]. The concentration of chromium ions in drinking water
allowed by the World Health Organization (WHO) is 0.05 mg/L and into inland surface water is 0.1 mg/L [4]. Thus, the removal of chromium ions in chrome electroplating wastewater with adsorption process is becoming a crucial issue. Due to the simple to operate for removing trace levels of chromium ions is adsorption method [5].

Adsorbent prepared from bovine bone is an alternative adsorbent as substitute of activated carbon synthesis has been familiar, because of its preparation, regeneration and reactivation procedures known expensive economically as well as degradable for little [6]. The adsorbent from bovine bone has criteria, there is higher adsorption ability, regenerable and reusable. Moreover, its source can be used bovine bone waste (waste of bovine bone handycraft) [7]. Optimization of adsorption ability of bovine bone by NaOH activated, in order to reduce pollutants of adsorbent pores so that increased both specific surface area and surface active sites. Adhi et al. [7] examined that the bone charcoal which was activated with 0.4 M NaOH, had increased adsorption ability to toxic content of textile dyes wastewater, as synthetic organic compound and heavy metals. Therefore, activating process of adsorbent is important.

Adhi et al. [7] studied the adsorption of charcoal powder activated 0.4 M NaOH as bio-inorganic sorbent to textile industrial dyes wastewater. It is showed that amount of surface acidity (active sites) and specific surface area of bovine bone activated 0.4 M NaOH had responsible to adsorption ability of the adsorbent toward physico-chemical properties of industrial dyes wastewater (degrees of turbidity, chemical oxygen demand (COD) and heavy metals content of Pb and Cr). Although the study of using charcoal from bovine bone for adsorption of dyes wastewater was often done, but just dominating studied adsorption capacity, not another characteristics of adsorption, likes parameter factors of temperatures effect (thermodynamics) have not been done yet. Whereas, it is important in increasing adsorption ability.

Base on that fact, the present study was attempted to determine adsorption characteristics of chromium ions in chrome electroplating wastewater by activated low cost adsorbent prepared from bovine bone waste, such as adsorption isotherms (various concentrations of chromium ions to adsorption ability) and adsorption thermodynamics (various temperatures in adsorption).

2. METHODS

2.1. Preparation and Characterization of Adsorbents

Bovine bone powder washed by H2O2 rinsed by distilled water for fading fate and other waste to remove water soluble materials at the surface. Then, filtered and dried in oven at 160°C for 12 hours [8]. Dried bovine bone powder was sieved to obtain a particle size range of 250-500 µm. It was carbonizated in tanur at 300°C for 1 hour, then labeled with AT. Furthermore, 60 g of charcoal powder put into Beaker glass, added 900 mL of 0.2 M NaOH solution and mixed with magnetic stirrer for 2.5 hours. Then, the mixture was filtered and its residue was washed by distilled water (free from OH- ions until negative test of pp indicator), dried thoroughly at range temperature 105-110°C in oven till reached constant weight and labeled by AT0.2, stored in glasses bottle and saved in desicator for further use. Similar procedure was done to activate with NaOH solution concentrations of 0.4; 0.6 and 0.8 M (labeled with AT0.4; AT0.6 and AT0.8, respectively). The adsorbents are analysed amount of surface active sites by acid-base titration method, crystallinity
and crystal size with X-ray diffraction (Shimadzu/XRD-6000), surface morphology and elementals composition by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS, JEOL JSM-6510 LA/Japan).

2.2. Effect of Contact Time Process

The batch adsorption experiments were conducted in seven of 100 mL Erlenmeyer flash where 0.3 g of the 

\( \text{AT}_{0.2} \) adsorbent as the highest amount of surface active sites and 25.0 mL of the sample of chrome electroplating wastewater was added, then mixed with magnetic stirrer for 30, 60, 120, 180, 240 and 300 minutes and filtered with Whatman filter papers. The concentration of chromium ions in filtrate is measured by atomic absorption spectrophotometer (AAS, Shimadzu/AA-7000 series) at wavelength \( \lambda \) of 357.87 nm to get adsorption capacity \( Q_{ads}, \text{mg/g} \) calculated by equation of

\[
Q_{ads} = \frac{(C_o - C_e)V}{m}
\]

Where, \( C_o \) and \( C_e \) are the initial concentration of chromium ions and at equilibrium (mg/L) respectively, \( V \) is the volume of the solution (L) and \( Q_{ads} \) is the amount of chromium ions adsorbed (mg) per mass unit of adsorbent (g) [9, 10]. Similar measurements were investigated to adsorbents of \( \text{AT}_{0.4}, \text{AT}_{0.6} \) and \( \text{AT}_{0.8} \) as well as AT adsorbent (as a comparison). Effect of contact time was showed by plotting between various contact times and amount of chromium ions adsorbed.

2.3. Adsorption Isotherm Process

In each of three Erlenmeyer flash of 100 mL where 0.3 g of \( \text{AT}_{0.2} \) adsorbent and 25.0 mL of the sample of chrome electroplating wastewater concentrations of 10, 20, 30, 40, 45 and 50 mg/L was added, then mixed with magnetic stirrer for the optimum contact time and filtered with Whatman filter papers. The concentration of chromium ions in filtrate are measured by AAS at \( \lambda \) of 357.87 nm to obtain adsorption capacity \( Q_{ads}, \text{mg/g} \). Afterward, from the extrapolation of the adsorption isotherm models of Langmuir and Freundlich, can be determined. Langmuir adsorption isotherm model is measured by plotting \( \frac{C}{Q_{ads}} \) versus \( C_e \), while Freundlich adsorption isotherm model by plotting \( \log Q_{ads} \) versus \( \log C_e \). These models are more applicable determined by the straight line in the graph [10, 11].

2.4. Adsorption Thermodynamics Process

In each 0.30 g of AT, \( \text{AT}_{0.2}, \text{AT}_{0.4}, \text{AT}_{0.6} \) and \( \text{AT}_{0.8} \) adsorbents were entered into Erlenmeyer flash of 100 mL and added with 25.0 mL of chrome electroplating wastewater sample of concentration which obtained from adsorption isotherm process. Each mixture were agitated for optimum contact time at various absolute temperatures i.e. 300, 305, 310 and 315 K. Then, adsorbents were filtrated with Whatman filter papers. The concentration of chromium ions in filtrate was measured by AAS at \( \lambda \) of 357.87 nm to obtain adsorption capacity \( Q_{ads}, \text{mg/g} \). The standard Gibbs free energy \( (\Delta G^o) \) in each temperature is calculated by terms of \( \Delta G^o = -RT \ln K_c \) [12, 13, 14]. Where, \( R \) is universal gas constant \( (8.314 \text{ J/mol/K}) \), \( K_c \) is thermodynamics equilibrium constant and \( T \) is absolute temperature (K). The thermodynamics equilibrium constant \( (K_c) \) is calculated by

\[
K_c = \frac{C_{ads}}{C_e}
\]

Where, \( C_{ads} \) and \( C_e \) are the concentration of chromium ions adsorbed and at the equilibrium, respectively [15]. Determination of the standard enthalpy change \( (\Delta H^o) \) and the standard entropy

\[
\Delta H^o = \Delta G^o + RT
\]
change (ΔS°) were plotted between ΔG° and T based on the equation of ΔG° = ΔH° - TΔS° [9, 10, 14], so that the straight line in the graph with -ΔS° as a slope and ΔH° as an intercept.

3. Results and Discussion

3.1. Amount of Surface Active Sites Of Adsorbents

The amount of surface active sites of adsorbents are presented in Table 1.

Table 1: The amount of surface active sites of adsorbents

| Adsorbent | Amount of surface active sites (sites/g) |
|-----------|----------------------------------------|
| AT        | 7.974 x 10²⁰                           |
| AT₀.₂     | 7.190 x 10²⁰                           |
| AT₀.₄     | 8.030 x 10²⁰                           |
| AT₀.₆     | 7.146 x 10²⁰                           |
| AT₀.₈     | 7.469 x 10²⁰                           |

Based on Table 1, the amount of surface active sites are the highest on 0.4 M NaOH activated charcoal adsorbent (AT₀.₄), different 5.6 x 10¹⁸ sites/g than AT adsorbent. The activation dissolved contaminant in the pores so that these are became more opened and increased amount of surface active sites. Adhi et al. (2017), reported that the activation to charcoal of bovine bone showed the functional groups of O-H bending appear at wavenumber of 742.59 cm⁻¹ but without activation is not appear. It means that the Bronsted acid sites tend to increase and linear with surface acidity (increased from 0.60 to 0.73 mmol/g) [7].

3.2. Crystallinity and Crystal Size of Adsorbents

The XRD pattens of adsorbents without and with 0.4 M NaOH activated (AT and AT₀.₄) (Fig. 1), tend toward semicrystalline to crystalline with intensity at 2θ = 32° decreased from 252 to 217 counts and 2θ = 33° from 112 to 109 counts. Its meaning, the activation on charcoal with 0.4 M NaOH concentration causes the mouth of pores getting more opened, so that increasing specific surface area. According to Adhi et al. (2017), the activation to charcoal of bovine bone can enhance spesific surface area from 10.19 to 20.08 m²/g [7].

Figure 1: XRD patterns of adsorbents
The 2θ angle range between 26 to 33° is the region of apatite phase, such as calcium hydroxyapatite of 2θ angle from 26 to 32° and hydroxyl carbonat apatite of 2θ angle at 33°. Activating process of adsorbent with 0.4 M NaOH shifted 2θ angles at 29.09, 32.31 and 33.24° on AT adsorbent to 26.21, 32.41 and 33.28° on AT0.4 adsorbent, respectively. Intensity of 2θ angle from 32 to 33° decreased due to cationics substitution (Na+ ions substitute Ca2+ ions) and/or elementals decomposition (dissolved carbonat) in the apatite structure [16, 17].

The mean crystal size of adsorbents were calculated by Scherrer’s aquation of \( L = \frac{k\lambda}{\beta\cos\theta} \) [18], where \( L \) is mean crystal size, \( k \) is Scherrer constant (maximum 1.0), \( \lambda \) is wavelength of X-ray diffraction (CuKα-radiation of 1.5406 Å), \( \beta \) is full width at half maximum (FWHM) its maximum intensity (2θ angle at 32°) and \( \theta \) is angle of diffraction.

| Adsorbent | Mean crystal size (nm) |
|-----------|------------------------|
| AT        | 6.655                  |
| AT0.4     | 7.567                  |

The mean crystal size of adsorbents (Table 2) increased due to 0.4 M NaOH activated. Activating process increased crystallinity and crystal size. In the nanomaterial terminology, AT and AT0.4 adsorbents are nanocristalline catagory because crystalline material that have an average crystal size between 1 and 100 nanometers [5].

### 3.3. Surface Morphology and Elementals Composition of Adsorbents

Surface morphology of adsorbent without and with 0.4 M NaOH activated are showed in Fig. 2. SEM image of AT adsorbent described that the pores and topography more uniform than AT0.4 adsorbent but particle sizes bigger than AT adsorbent. The adsorbents exhibit rough and uneven surface morphology [19]. It means that stack of agglomerates of particle occur which make particle sizes bigger. This phenomenon was agreement with mean crystal size which is calculated by Scherrer’s aquation (Table 2).

![Figure 2: SEM images of surface morphology of adsorbents at 3000x enlargement](image-url)
The result of EDS analysis (Fig. 3), showed that relative elemental composition of AT adsorbent were C (15.55%), O (44.42%), Na (0.74%), Mg (0.67%), P (12.54%) and Ca (26.09%) while for AT\textsubscript{0.4} adsorbent were C (13.52%), O (46.09%), Na (1.22%), P (14.21%) and Ca (24.96%). Activating process with 0.4 M NaOH leached both Mg and Ca due to the increase Na. Leaching Mg because of dissolving Mg with NaOH activator and Ca cations were exchanged by Na. This process to become pore more opened and increasing amount of surface active sites (Table 1). The ratio of Ca/P of AT and AT\textsubscript{0.4} adsorbents were 2.08 and 1.76, respectively. The ratio of Ca/P of AT\textsubscript{0.4} adsorbent more close than standard hydroxyapatite (1.67), which indicates that the structure of AT adsorbent close and more basic properties compared AT\textsubscript{0.4} adsorbent\textsuperscript{[16, 18, 20]}. This result was agreement with amount of surface active sites (see in Table 1).

### 3.4. Test of Adsorption Process: The Optimum Contact Time

The AT\textsubscript{0.4} adsorbent is used to determine the optimum contact time of adsorption toward chromium ions in chrome electroplating wastewater because it has the highest amount of surface active sites, so that interaction time needed faster for equilibrium than another one. The plots of optimum contact time toward amount of chromium ions adsorbed was described in Fig. 4.
Fig. 4 presents that contact time of 180 minutes able the highest to adsorb chromium ions in chrome electroplating wastewater was 0.9147 mg/g and decrease to 0.8561 mg/g (reduce 5.86%) and 0.7231 mg/g (reduce 19.16%), when it is interacted for 240 and 300 minutes, respectively. Its meaning, those indicated that reached equilibrium state. Therefore, contact time of 180 minutes as an optimum contact time to this adsorption process.

3.5. Test of Adsorption Process: The Optimum Concentration

In Fig. 5, adsorption of chromium ions in chrome electroplating wastewater with AT_{0.4} adsorbent increased at initial concentrations from 10 to 45 mg/L and adsorbed from 0.19 to 0.63 mg/g, respectively. The amount of chromium ions adsorbed had decreased (0.53 mg/g) at initial concentration of 50 mg/L. Therefore, chromium ion at initial concentration of 45 mg/L is chosen as an optimum concentration of adsorption in determination of thermodynamic parameters (∆G°, ∆H° and ∆S°).

![Figure 5: The plots of optimum adsorption concentration of AT_{0.4} adsorbent adsorbing chromium ions in chrome electroplating wastewater](image)

3.6. Test of Adsorption Process: Adsorption Isotherms

Chromium ions in chrome electroplating wastewater was adsorbed by AT_{0.4} adsorbent well agreement Freundlich adsorption isotherm model (Fig. 7) of correlation coefficients (R²) is 0.8008 bigger than Langmuir model (0.2644) given in Fig. 6. It means that the AT_{0.4} adsorbent had heterogeneous surface, physically interaction and described multilayer adsorption [10, 18, 19, 21].

![Figure 6: The Langmuir adsorption isotherm model at optimum contact time of 180 minutes and initial chrome electroplating wastewater at optimum concentration of 45 mg/L](image)
3.7. Test of Adsorption Process: Adsorption Thermodynamics

Thermodynamic parameters including the standard Gibbs free energy ($\Delta G^0$), the standard enthalpy change ($\Delta H^0$) and the standard entropy change ($\Delta S^0$) for adsorption of chromium ions in chrome electroplating wastewater by adsorbents without and with NaOH activated are summarized in Table 3.

Table 3: The amount of chromium ions adsorbed ($Q_{ads}$), the standard Gibbs free energy ($\Delta G^0$), the standard enthalpy change ($\Delta H^0$) and the standard entropy change ($\Delta S^0$)

| Adsorbent | Absolute temperature (K) | $Q_{ads}$ (mg/g) | $\Delta G^0$ (kJ/mol) | $\Delta H^0$ (kJ/mol) | $\Delta S^0$ (kJ/mol) |
|-----------|--------------------------|------------------|-----------------------|-----------------------|-----------------------|
| AT        | 300                      | 0.8800           | 3.1554                | -42.93                | -0.153                |
|           | 305                      | 0.7178           | 3.8442                |                       |                       |
|           | 310                      | 0.5870           | 4.5354                |                       |                       |
|           | 315                      | 0.4389           | 5.4816                |                       |                       |
| AT$_{0.2}$ | 300                     | 0.8578           | 3.2365                | -28.26                | -0.104                |
|           | 305                      | 0.7913           | 3.5481                |                       |                       |
|           | 310                      | 0.6929           | 4.0274                |                       |                       |
|           | 315                      | 0.5475           | 4.8206                |                       |                       |
| AT$_{0.4}$ | 300                     | 0.9110           | 3.0439                | 31.00                 | 0.093                 |
|           | 305                      | 1.0776           | 2.5282                |                       |                       |
|           | 310                      | 1.1681           | 2.2810                |                       |                       |
|           | 315                      | 1.4161           | 1.5734                |                       |                       |
| AT$_{0.6}$ | 300                     | 0.8733           | 3.1796                | -122.20               | -0.416                |
|           | 305                      | 0.6969           | 4.3483                |                       |                       |
|           | 310                      | 0.3800           | 5.8088                |                       |                       |
|           | 315                      | 0.0985           | 9.6297                |                       |                       |
| AT$_{0.8}$ | 300                     | 0.8290           | 3.3445                | -191.40               | -0.645                |
|           | 305                      | 0.5307           | 4.7604                |                       |                       |
|           | 310                      | 0.2470           | 7.0132                |                       |                       |
|           | 315                      | 0.0241           | 13.3551               |                       |                       |
Table 3 showed that the amount of chromium ions adsorbed (Q_{ads}) by adsorbents without and with NaOH activated are the highest on AT_{0.4} adsorbent, increased linear with increasing temperatures. Meanwhile, the another adsorbents are contradictory. The adsorption chromium ions in chrome electroplating wastewater on adsorbents at various temperatures were endothermic (positive value of \Delta G^\circ). It means that the bond between adsorbent and chromium ions (adsorbate) were leaching easily (desorption). Increasing adsorption temperature made to enhance \Delta G^\circ because of the adsorbate is desorbed easily. Data in Table 3 showed that adsorption adsorbents at various temperatures are catagorised as a physical adsorption, because the value of \Delta G^\circ less than 20 kJ/mol [10, 14]. This phenomena suitable for Freundlich adsorption isotherm model (see in Fig. 7) indicated physical adsorption. The positive value of \Delta H^\circ and \Delta S^\circ cause spontaneous exchange in high temperature. The positive value of \Delta S related to bonding strength in adsorbate and the increase randomness of solid/solution interface during adsorption process [6, 22]. Opposite the negative value of \Delta H^\circ and \Delta S^\circ indicate occur spontaneous exchange in low temperature [14, 22]. Base on Table 3, adsorption process on AT_{0.4} adsorbent tend to be spontaneous process while another adsorbents non-spontaneous.

4. Conclusions

In this work, the adsorbent characteristics such us the highest amount of active sites because of NaOH activated at 0.4 M concentration on adsorbent prepared from bovine bone waste (AT_{0.4}) was 8.030 x 10^{20} sites/g. Crystal size increased from 6.655 to 7.567 nm with surface morphology was agglomerates and leached both Mg and Ca due to the increase Na. The adsorption of adsorbent without and with NaOH activated to chromium ions in chrome electroplating wastewater was the highest adsorption ability on AT_{0.4} adsorbent well agreement with equilibrium isotherm described by Freundlich model as indicating physical adsorption and non-spontaneous process. Specifically, for AT_{0.4} adsorbent had the tendency to be spontaneous process.

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