Chromium removal from chrome-tannery effluent after alkaline precipitation by adsorption using municipal solid waste-derived activated biochar

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Abstract. Municipal solid wastes (MSW) accumulation and generation of toxic wastewater are common issues especially in highly industrialized and urban communities. To address these concerns, municipal solid wastes was converted to activated biochar (MSWAB), which can be used to treat alkaline-precipitated tannery wastewater by adsorption to meet the environmental limit of 0.5 ppm Cr\textsubscript{total} concentration. Alkali precipitated tannery wastewater has an initial Cr\textsubscript{total} concentration of about 3364.37. MSW pyrolysis at 500°C for 30 mins produced about 50.42 % w/w biochar, which was activated using KOH to improve its adsorption capacity. Equilibrium time for Cr adsorption using MSWAB was established after 1 hour of adsorption. The effect of pH and adsorbent dosage on the Cr\textsubscript{total} removal were then tested from pH 6.5 to 12 and from 0.2 to 10 mg MSWAB/ mL wastewater, respectively, using 2x factorial design. Statistical results show that both factors were significant on the percent removal of Cr\textsubscript{total}. Maximum Cr\textsubscript{total} removal obtained was about 98.97% using MSWAB as adsorbent at pH 12 with 10 mg/mL dosage. Freundlich isotherm best described the adsorption of Cr onto MSWAB (R\textsuperscript{2} = 0.8231) as compared to the Langmuir isotherm (R\textsuperscript{2} = 0.5079). Commercial activated carbon (CAC) with a removal of 57.39 % was still observed to have higher removal efficiency compared to the 55 % removal using MSWAB at pH 8.5. However, considering the low cost of feedstock used, environmental benefits, and its adsorption performance, MSWAB can be a possible alternative for CAC.

1. Introduction
Rapid population growth coupled by urbanization and economic development results to a higher accumulation of solid wastes, which poses health and environmental problems especially if improperly disposed. Municipal solid wastes or MSW includes plastics, food wastes, yard wastes, and paper wastes which come from residential, commercial, and industrial sources. In the Philippines, MSW should be disposed properly in sanitary landfills as mandated on the Ecological Solid Waste Management Act of 2000 or Republic Act 9003 (RA 9003). However, at present, large fractions of MSW are still being disposed in open landfills thus contributing to the air, water, and land pollution. An increase from 37,426.46 tons to 40,087.45 tons per day of solid wastes was reported from 2012 to 2016 in the Philippines [1]. In 2020, this is expected to further increase to about 16.63 million tons [2]. Different methods of managing solid wastes are currently being practiced as mandated in RA 9003 such as recycling, source reduction, and composting [1]. Since landfills in the country are limited and are expected to reach full capacity soon, several studies have been conducted to utilize solid wastes and recover valuable materials and energy from the wastes.
MSW contains organic materials that have potential in storing energy. The stored energy when broken down via thermochemical and biochemical processes may produce solid, liquid, and gaseous materials which contains considerable amounts of energy and can be used as energy sources. One thermochemical technique is pyrolysis. Pyrolysis is a process by which thermochemical degradation occurs producing chars, oils, and combustible gases that can be used for other processes [4]. Chars produced can be activated and can be used for wastewater treatment. Activation of chars involves the use of chemicals or steam to enhance its porosity and adsorptive capacity. The use of chemically activated biochar has been developed since it is found to be efficient in the adsorption of heavy metals and metalloids, and the raw materials are low cost [5].

Chrome tanning process used in leather making produces effluents which contains toxic metal salts and metal ions. Basic Chromium Sulphite (BCS) is one of the chemicals being used in high amounts for the pre-treatment of animal hides and skins. Upon addition to solvent, a blue solution is formed which contains high levels of chromium, which commonly exists as Cr (III) or Cr (VI). Trivalent chromium or Cr (III) is an essential element in the body and other living organisms, however, can also be toxic in high amounts. It may cause skin allergies, respiratory problems, kidney and liver damage, weakening of immune system at certain concentration [6]. On the other hand, hexavalent chromium or Cr (VI) is much more toxic than the other form. Contact and intake of Cr (VI) can cause respiratory problems and cancer. Thus, treatment of chromium-containing wastes must be done prior to disposal. In the Philippines, tannery operation can be found in Bulacan which is said to be one of the reasons on the pollution of the Meycauayan-Marilao-Obando River System (MMORS). The river system was considered by the Blacksmith Institute as one of the top 30 dirtiest rivers in the world for the year 2008 [7]. In 2009, Dela Cruz as cited by Avena [8] studied the use of reduction-precipitation method for treatment of the tannery wastewater. The study involves optimizing chromium removal from actual tannery effluent using sodium sulphite as reducing agent and NaOH as precipitating agent. The first step involves reducing the hexavalent chromium (Cr6+) to trivalent chromium (Cr3+) using sodium sulphite as reducing agent. This was followed by chemical precipitation using NaOH as precipitating agent to remove chromium from the effluent. The chemical precipitation was able to reduce the initial total concentration of chromium from 2230 ppm into 13 ppm. This amount of total chromium concentration, however, is still greater than the 0.5 ppm residual total chromium concentration limit set by the Department of Environment and Natural Resources.

Chromium removal from tannery effluent using agricultural wastes derived activated carbon was studied by Avena [8] and Bondoc [9]. In the study of Avena [8], cacao pod husk was used as the feedstock for producing activated carbon which was tested as adsorbent for chromium. Two factors are considered in the experiment, adsorbent dosage and pH concentration, which were found to have significant effect on the residual Cr total concentration during adsorption. In his study, the optimum conditions were adsorbent dosage of 0.01592 g/mL and pH 9, which resulted to high chromium removal of about 95.89%. At the optimum condition, it was also found out that cacao pod husk activated carbon is more efficient and effective than the commercially available activated carbon [9]. Durian shells were the primary source of activated carbon made by Bondoc [9]. Similar to the study of Avena [8], two factors were tested - adsorbent dosage and pH. These two factors were also found to have a significant effect on chromium removal. Optimum conditions for the durian shell activated carbon were 9.8 mg/mL adsorbent dosage and pH of 8.56 resulting to 98.35 % chromium removal. The durian shell-derived activated carbon was also compared to the commercial activated carbon under optimum conditions and was found out to be more effective than the latter [9]. The two activated carbon derived in these studies were said to be potential alternatives to the commercially available activated carbon.

Other similar studies for chromium removal using activated carbon were conducted by Labied et al [10] and Chen et al [11]. Hence, this study aimed to develop a process that utilizes municipal solid wastes as feedstock for the production of activated biochar via pyrolysis. The MSW activated biochar was then used to treat chromium-contaminated tannery effluent through adsorption after alkaline precipitation. The characteristics of the activated biochar were evaluated first in terms of morphology and pore size. The
yield of raw and activated biochar were also computed. The activated biochar was then used in the adsorption experiment to determine the effect of pH and adsorbent dosage on Cr removal from alkaline precipitated actual tannery effluent. Optimized conditions for maximum percent reduction of chromium concentration was determined using Response Surface Methodology (RSM). The adsorption isotherm for Cr adsorption onto MSWAB was determined under optimum conditions. Lastly, the activated biochar was compared to commercial activated carbon in terms of cost and adsorption efficiency to assess its potential as an alternative adsorbent.

2. Materials and Methods

2.1. Preparation of MSW-derived biochar

Municipal solid wastes (MSW) were collected from residential and commercial area around Los Banos, Laguna, Philippines. MSW consisting of papers, plastics, food wastes, and yard wastes were sun-dried for 3 days then were put in an oven dryer for 48 hrs at 60 °C. Materials such as batteries and other metals found in the MSW were discarded to avoid possible unwanted reactions. After the drying process, the dried MSW were fed to a Multi-Purpose shredder and hammer mill. A USA standard testing sieve with Mesh -16 + 30 (particle size: 0.60 mm to 1.18 mm) was used to isolate the desired particle size. Each type of MSW was separately size reduced and screened. The components were mixed in a plastic container to achieve uniformity in the distribution of the different MSW. Mixed MSW were kept at room temperature in an air tight container to avoid accumulation of moisture.

For carbonization of MSW, stainless steel reactors with 7 cm height, 6 cm diameter, and 0.25 cm thickness were used [8]. About 50 g of MSW was placed in each reactor with holes by which nitrogen gas was purged for 2 minutes to remove the oxygen content. All reactors containing MSW were put inside a Vulcan A-550 furnace and heated to 500 °C. Upon reaching the desired temperature, the MSW were pyrolyzed for 30 mins. Biochar obtained was cooled inside the furnace to room temperature and stored in an airtight plastic container [9].

2.2. MSW Biochar Activation and Characterization

MSW biochar was subjected to chemical activation. Following the methods of Jin et al. [5], 25 g of biochar was mixed and stirred with 100 mL of a 2 M potassium hydroxide (KOH) solution for 1 hr. It was filtered using filter paper then washed with diluted HCl solution and distilled water until the pH became stable or neutral. The mixture was filtered again to recover the activated biochar and then dried in a hot plate at 105 °C. The recovered dried MSW activated biochar (MSWAB) was stored in an airtight container.

The MSW biochar and activated biochar were characterized in terms of surface area and pore size. The surface area was determined using nitrogen sorption analysis and estimated by the Brunauer-Emmett-Teller (BET) model. This was done using Micromeritics Gemini VII 2390 Surface Area Analyzer at 77 K. The sample was vacuum-dried for 12 hours and degassed for 3 hours at 150 °C so that excess volatile compounds will be removed. A relative pressure range (P/Po) of 0.5 to 0.30 was used to determine the specific surface area. Actual photographs of the surface of the biochar were taken by Scanning Electron Microscope (SEM). The samples, coated with 10-nm layer of gold/palladium using BAL-TEC MED 020, were prepared by depositing onto SEM sample stubs with aluminum tape. The micrographs were captured using Zeiss Ultra Plus Field Emission-Scanning Electron Microscope in a high vacuum mode at an acceleration voltage of 5kV with 30μm aperture size using InLens secondary electron detector.

2.3. Collection of Tannery Wastewater

The wastewater sample was collected from a local tannery and was filtered to remove excess solids. The initial pH of the sample was measured using the calibrated pH pen. Due to its high concentration, a dilution factor of 1:25 (v/v) was made to easily read its chromium concentration under Flame Atomic Absorption Spectrophotometer (FAAS). The wastewater sample was stored at room temperature.
2.4. Precipitation of Cr (III) from Tannery Wastewater
Tannery wastewater samples were diluted at a ratio of 1:25 (v/v). Alkaline precipitation at pH 8.5 was done to reduce the Cr\text{total} concentration based from the study of Dela Cruz [10]. Drops of 50 % wt/v NaOH were added to the sample with constant stirring using Corning PC-620D magnetic stirrer operating at 500 rpm until said pH was reached. The solution was filtered and stored in a covered chemical container. The residual Cr\text{total} concentration was measured using Flame Atomic Absorption Spectrophotometer (FAAS).

2.5. Determination of Equilibrium Time for Adsorption
Different adsorbent dosage of MSWAB were set to 1 and 10 mg MSWAB/mL Cr solution. A 100 mL wastewater sample was mixed with the given amount of biochar (0.1 g and 1 g) in a 250 mL Erlenmeyer flask with constant stirring using a table top shaker. Seven samples were prepared for each dosage corresponding to the different time intervals that were used. The 14 samples were run altogether under the same condition. Different time intervals were set (5 min, 10 min, 20 min, 30 min, 60 min, 120 min, 150 min) to determine the equilibrium time. The solution was filtered after each run and was stored in a vial then subjected to FAAS for the reading of the Cr\text{total} concentration. The residual Cr concentration was then plotted against time and the time at which the concentration became constant was considered as the equilibrium time for Cr adsorption.

2.6. Experimental design
For the parametric analysis of the study, 2k factorial was applied using Design Expert 11. Two factors, which are adsorbent dosage and pH, were tested if they have significant effect on Cr removal during adsorption. For the pH, the low value was set at 6.5 and the high value at 12. The pH of the solution was adjusted using 10% (v/v) H2SO4 and 1 M NaOH. Some precipitates were formed after addition of NaOH, thus filtration was done.

For the adsorbent dosage, 0.2 mg MSWAB/mL solution and 10 mg MSWAB/mL solution were used for the adsorption of 100 mL wastewater based from the parametric study done by Bondoc [11].

2.7. Determination of Adsorption Isotherm
Different adsorbent dosages were used for the determination of adsorption isotherm. Following the method of Avena [8], adsorbent dosage used were 0.01, 0.05, 0.1, 0.150, and 0.2 mg MSWAB/ml solution. A 100 ml solution was used for the adsorption isotherm experiment at pH 8.5. The samples were put in the table top shaker for 1 hour for the adsorption. After 1 hour of adsorption, the samples were filtered and then tested using FAAS for the determination of Cr concentration. Data obtained were used to determine the appropriate isotherm using best fit curve. The adsorptive capacity or q_e, and the equilibrium concentration or C_e were needed for the equation. Data were used to fit for Freundlich and Langmuir, isotherm using equations (1) and (2) respectively. The equation with the higher R^2 obtained was considered as the best isotherm fit for the adsorption.

\[ q_e = K C_e^n \]  

where

- \( q_e \) is the adsorptive capacity
- \( C_e \) is the equilibrium concentration
\[ n \text{ and } K \text{ are constants} \]

\[ q_e = \frac{q_mC_e}{1+KC_e} \quad (2) \]

where

- \( q_e \) is the mass of adsorbed particles per unit mass of the original adsorbent
- \( C_e \) is the equilibrium concentration
- \( q_M \) is the maximum adsorptive capacity
- \( m \) is the mass of the adsorbent
- \( K \) is the Langmuir constant

2.8. Comparison of CAC and MSWAB

MSW derived activated biochar was compared to commercial activated carbon (CAC) in terms of their adsorptive capacity or \( q_e \). Three replicates of 50 ml wastewater sample (pH 8.5) with adsorbent dosage of 10 mg MSWAB/mL Cr solution were prepared. After adsorption, the sample was subjected to FAAS analysis for the final equilibrium concentration to determine the adsorptive capacity of both the MSWAB and the CAC. The actual wastewater sample was tested to determine if it follows the guideline set by DENR DAO 2016-08 for water quality.

3. Results and Discussion

3.1. Yield and Characteristics of the MSW Biochar and Activated Biochar

From a 50 g sample of MSW, 25.204 g of biochar was recovered, which corresponds to about 50.42 \% (w/w) yield. The low production yield may be due to the release of volatile substances and formation of pores in the surface of the biochar. Potassium hydroxide (KOH) was used for biochar activation. According to Genuino et al. [9], this is the most widely used chemical activating agent and it increases the surface area and forms functional groups of –OH on the surface of the carbon. Activation using KOH results to micropores which is good for adsorption of micropollutants and heavy metals [12]. Three mechanisms can explain the formation of pore network upon activation [9]. The first mechanism is the etching of the solid structure caused by the reactions formed between species of carbon and potassium. The second mechanism involves KOH dehydration forming H₂O and CO₂ that cause carbon gasification leading to pore development. Lastly, pore development is due to intercalation of metallic K in the framework that results to the development of carbon lattice resulting to formation of micropores. The recovered biochar from the previous step was allowed to be soaked in KOH for 1 hour then dried at 105 °C. After the activation, 98.76 \% activated biochar was recovered. The approximately 2 \% loss was probably due to the destruction of the pores caused by activation.

The activation enhanced the surface area of the biochar. The biochar obtained from pyrolysis of MSW has a surface area of about 2.6 m²/g which increased to about 6.5 m²/g after activation. However, this value is still low relative to the literature value from Jin et al. [5] which is 49.1 m²/g. According to Mopoung et al. [13], the low BET surface area may be due to the formation of K₂CO₃ and other similar compounds from the activation using KOH. These potassium-rich compounds cover the surface of the activated biochar thus giving a low BET surface area. The slight increase of the surface area after activation may be attributed to the destruction of nanopores into mesopores due to etching of KOH [5]. Also, the presence of inorganic materials such as glass and sand could have affected the porosity of the sample since these two are non-porous and may affect the adsorption ability of the biochar.
Micrographs of the surface of MSW biochar were captured using Scanning Electron Microscope (SEM). The micrographs obtained were compared with other micrographs obtained from other literature with the same magnification. Shown in Figure 1 are the micrographs of a coconut shell biochar and the obtained micrograph of MSW both at 800x magnification.

(a)  
(b)  

Figure 1. SEM Images of the biochar: (a) Coconut shell biochar from Devens et.al [14] (b) MSW biochar.

One of the components of the MSW is organic wastes which is composed primarily of coconut shells. Comparing the two micrographs presented above (both with 800x magnification), similar structure can be observed, thus fraction captured by SEM may be assumed to be similar to a coconut shell-derived biochar. Cylindrical tubes forming a honeycomb-like structure can be observed which signify complex networks of pores. The vascular bundle shape and the internal pore formation of this certain component of the MSW biochar is a good quality for the adsorption of contaminants [14].

The process done to produce the MSW biochar was slow pyrolysis. This process results to the release and destruction of the volatile substances such as organic matter, hemicellulose, and lignin, thus increasing the porosity of the samples [15]. Since limited pore count has been made in the sample, the increase in pore size due to activation cannot be generalized, thus the effect of activation can only be compared using the surface area determination using the nitrogen sorption analysis.

Shown in Figure 2 are the SEM micrographs of MSW activated biochar. The first micrograph (Figure 2a) is an MSW derived activated biochar by Gopu et al. [16] which is pyrolyzed at 408 °C and activated at 600 °C with an S_{BET} of 8.3 m²/g. On the other hand, Figure 2b is the micrograph of the activated biochar produced in this study at 500 °C pyrolysis. The two micrographs show similarity in structures which are observed to be in “clump” and with minimal porosity. The minimal porous structure observed can be attributed to the low S_{BET} obtained in the nitrogen sorption analysis.
3.2. Chromium Concentration of Tannery Wastewater

The raw tannery wastewater has high amount of chromium with a concentration of about 3364.37 ppm which could be Cr (III) as indicated by the blue color of the solution. After alkaline precipitation, only about 11.86 ppm was left in the solution which may be composed primarily of Cr (III) ions since most of the Cr (VI) was removed with or without the application of reducing agent [10]. However, although 99.65% of the total chromium concentration was reduced after alkaline precipitation, the residual Cr concentration still needs further reduction in concentration to meet the environmental limit of 0.5 ppm. Thus, a polishing treatment is needed; in this case, adsorption process must be done with the use of MSWAB as adsorbent. After alkaline precipitation, a clear and colorless liquid was derived.

3.3. Equilibrium Time for Adsorption

Determination of equilibrium time was done first in order to know the shaking time for all adsorption experiment. This is the time by which the Cr concentration starts to become constant. Adsorbent dosage used for the equilibrium time determination was based from the study of Avena [8] and Bondoc [11]. The two dosages (1 mg/mL and 10 mg/mL) were used to see significant results on the adsorption process. Samples were run simultaneously in a table top shaker for 2.5 hours.

Figure 3 shows the relationship between the residual chromium concentration and time. For the higher dosage (10 mg MSWAB/mL Cr solution), the lowest residual chromium concentration is at t<20 minutes. On the other hand, the lower dosage reached its lowest peak at t=30 minutes. Adsorption of chromium is higher at the start due to larger surface area available at the start [17]. Active sites are freshly available at the start of adsorption thus high amounts of adsorbate were attracted. Andaya, as cited by Avena [8] studied the three stages of equilibrium time of adsorption. The first stage is the curve with the higher slope which is called the “external mass transfer stage”. At this stage, adsorbates are easily attracted to the sorbent due to the availability of the binding sites. After this stage, there is a time by which the residual concentration of the adsorbate increases. Desorption happens at the same time the adsorption occurs. This stage is the “adsorption-desorption stage”. Since active sites on the surface pores are limited now at this stage, some particles are being removed to the surface back to the solution, thus desorption happens. This phenomenon as observed in the graph (for 1 mg/mL dosage at t=30 mins and for 10 mg/mL dosage at t=15 mins) happens if the adsorbent has a weak attraction [18]. The last stage is
the equilibrium stage. After the adsorption-desorption stage, the residual concentration reaches its equilibrium. At this stage, the rate of adsorption is equal to the rate of desorption.

The three stages can be seen in the performance of the MSWAB at different time. Due to its low porosity, MSWAB can be considered as weak adsorbent thus the second stage can be observed. The two adsorbent dosages exhibited a constant behavior at t=60 minutes, thus it was considered as the equilibrium time of adsorption for chromium removal.

3.4. Factors Affecting Chromium Adsorption onto MSW Activated Biochar

The effect of the two factors, pH and adsorbent dosage, together with their interaction on Cr removal by MSWAB via adsorption was determined using the 2k factorial. With a p-value less than 0.0001 obtained, the model generated was significant. Moreover, the main effects (pH and adsorbent dosage) together with their interaction were found to be significant with p-values less than 0.0001. ANOVA assumptions were satisfied indicating significance of the parametric analysis.

3.4.1. Effect of pH

Generally, the percent chromium removal increases as the pH increases indicating that the residual chromium decreased as shown in Figure 4. Several factors such as Cr (VI) reduction, protonation and deprotonation of binding sites, and adsorption of metals due to solubility at various pH values affect the removal of chromium [11]. Total chromium content of the solution may be in two forms, the trivalent and hexavalent chromium. Trivalent chromium can exist as Cr³⁺, CrOH⁺, and CrOH₂⁺ under acidic condition while hexavalent chromium can be in the form of HCrO₄⁻, and Cr₂O₇²⁻ [19]. Since KOH was used for the activation of MSWB, the surface of the adsorbent became negative thus more positive ions may be attracted to the surface. Cr (III) as cation, however, may “compete” with the H⁺ ions to the negative surface of the adsorbent. Also, the positive ions from the environment cancel out the negative surface of the adsorbent thus attraction of positive ions is possible [19]. On the other hand, Cr (VI) exists as anion at this condition such as HCrO₄⁻, and Cr₂O₇²⁻. At lower pH, Cr₂O₇²⁻ is reduced to Cr³⁺ (given by Equation (3)) thus adding to the attracted species in the adsorbent (Attia et al., 2009).

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \tag{3}
\]

At basic condition, the negative charge of the surface of the adsorbent tends to repel the basic property of the solution thus positively charged ions are easily attracted to the negative surface. Existing Cr (III) species may be attracted to the surface while Cr (VI) species tends to contribute to the repulsive forces in the solution. At higher pH also, insoluble hydroxide precipitates may be formed which can be trapped on the surface of the adsorbent [17].

3.4.2. Effect of adsorbent dosage

Higher adsorbent dosage, on the other hand, gives higher Cr removal (Figure 4) since more active sites are available for adsorption. The increase in Cr adsorption at higher adsorbent dosage may be due to the increase in the surface area of the material and the availability of active sites for adsorption [20].

3.4.3. Effect of pH and adsorbent dosage
Varying the dosage of the adsorbent gives positive effect as the pH increases. As both factors are increased, the amount of chromium removed increases. More binding sites are available at higher pH and higher adsorbent dosage. At lower pH, however, the solution releases H⁺, which may compete with the adsorption of Cr (III) cations onto the limited active binding sites. Higher amount of adsorbent dosage at high pH gave higher removal since more surface and binding sites are available.

At low adsorbent dosage (black line), the effect on the % Cr removal at increasing pH is more evident than at higher adsorbent dosage (red line) as illustrated by the steeper line generated in the model presented in Figure 4. This effect can be attributed to the efficiency of the adsorbent to uptake heavy metals easily even at lower dosage. Increasing the pH of the solution was also observed to have larger effect on the % Cr removal as compared to the adsorbent dosage. Higher pH and adsorbent dosage give higher removal since attractive forces between adsorbent and adsorbate were governing due to presence of high amount of OH⁻ and the negative surface of the adsorbent thus Cr (III) were attracted.

From the results, maximum Cr removal (98.97%) can be achieved at pH 12 with adsorbent dosage of 10 mg MSWAB/mL wastewater resulting to residual Cr concentration of about 0.12 ppm Cr total concentration. The said concentration is lower than the 0.5 ppm environmental standards of the DENR; however, further treatment of the effluent by neutralization is necessary prior to disposal since the acceptable pH concentration must be within the range 6.5-9.

3.5. Isotherm for adsorption
The best isotherm for adsorption of Cr using MSWAB was also determined. Adsorption isotherms indicate the interaction of the adsorbates with the adsorbent at equilibrium [21]. The relationship between the loading, qₑ, and the equilibrium concentration Cₑ was obtained and plotted which is described by the isotherm. Each sample had different dosages at constant volume of wastewater and constant temperature. The samples were subjected for adsorption at pH 8.5 for 1 hour.
Langmuir and Freundlich isotherms are the commonly used model isotherms. Empirical constants are obtained and the linearized equations for the two isotherms were used for plotting the loading $q_e$ against the equilibrium concentration, $C_e$. The linearized equations for both Langmuir and Freundlich Isotherms and empirical constants obtained were presented in Table 1.

Table 1. Linearized equations and empirical constants for the Langmuir and Freundlich Isotherms.

| ISOTHERM | LINEARIZED EQUATION | $R^2$ | PARAMETER | VALUE  |
|----------|----------------------|-------|-----------|--------|
| Langmuir | $\frac{1}{q_e} = \left(\frac{1}{q_0} \right) \left(\frac{1}{K_L \cdot C_e} \right)$ | 0.5079 | $q_0$ | -5.2219 |
|          |                      |       | $K_L$    | -4.6695 |
| Freundlich | $\ln q_e = \ln K_f + \left(\frac{1}{n} \right) \ln C_e$ | 0.8231 | $\frac{1}{n}$ | 2.9965 |
|          |                      |       | $K_f$    | 0.2576  |

Based from the $R^2$ computed (Table 1), the best isotherm to describe Cr adsorption using MSWAB was the Freundlich isotherm with $R^2$ equal to 0.8231. Also, according to de Sa et al., as cited by Avena [8], the Freundlich isotherm are used for heterogeneous and multilayer adsorption, which best describes the Cr-MSWAB matrix, hence, the Freundlich isotherm was chosen. Higher values of $\frac{1}{n}$ and $K_f$ signify a higher uptake of metals [22]. Moreover, high value of $\frac{1}{n}$ indicates that even though at low adsorbent dosage was used, a large uptake of heavy metals can be observed.

3.6. Comparison of CAC and MSWAB

A slightly higher percent removal (57.59%) was observed using CAC compared to the 55.64% removal using MSWAB, which may be due to the lower surface area of the MSWAB relative to CAC. Further studies on improving the quality of MSWAB as adsorbent (i.e. varying pyrolysis temperature, activation conditions, etc.) can be done to make MSWAB comparable to CAC. Nonetheless, this result indicates that MSWAB can be a potential alternative for CAC if a low cost adsorbent is desired from renewable sources such as MSW.

4. Summary and Conclusion

In this study, activated biochar from municipal solid waste was used to further treat chrome tannery effluents through adsorption. Alkali precipitation was only able to reduce the chromium content of the wastewater to about 11.8625 ppm, which is still higher than the environmental limit (0.5 ppm), hence, a polishing treatment was deemed necessary. MSW activated biochar (MSWAB) was initially prepared using locally-sourced MSW as feedstock for pyrolysis followed by chemical activation using KOH. Characterization of MSWAB showed that its surface area is relatively low, which was attributed to the inorganic components of MSW, but comparable some literature values. Parametric analysis was done to determine the effects of two factors (pH and adsorbent dosage) on Cr removal during adsorption. Results showed that both pH and adsorbent dosage have positive significant effects on Cr removal factors. Generally, higher Cr removal was observed as pH is increased due to the electrostatic attraction of the adsorbent with Cr ions. On the other hand, higher adsorbent dosage resulted to more available binding sites for adsorption resulting to higher Cr removal. The highest % Cr removal obtained was 98.97% at pH 12 with dosage of 10 mg MSWAB/mL Cr solution which can be considered as the best condition for treatment of alkali precipitated chromium wastewater. Freundlich isotherm was found to be the isotherm that best describes the adsorption of Cr onto MSWAB. MSWAB was found to be still slightly inferior to CAC based on Cr removal, however, its low cost and the positive environmental
implications of using a renewable source such as MSW for the production of adsorbent may be beneficial.

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