Regeneration of Spent Activated Carbon from Wastewater Treatment Plant Application

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Abstract. The field spent activated carbon from the wastewater treatment plant application is vital to be regenerated for the reduction of environmental pollution, contribution of economic benefits and the preservation of the natural resources. In this study, chemical regeneration was identified by using hydrochloric acid and hot water to regenerate the spent activated carbon. The purpose of this study is to evaluate the adsorption capacity of regenerated spent activated carbon by chemical treatment; then develop a laboratory scale regeneration unit of spent activated carbon and subsequently characterize the activated carbon based on its pore structure and surface morphology. The adsorption capacity of the activated carbon were determined by the methylene blue number and iodine number. The optimal regeneration condition for activated carbon was found to be 0.05 M HCl, contact time of 360 minutes with 10 mL volume of HCl solution. The regeneration unit of the column was studied that the optimal flow rate is 1 mL/min. A micrographic analysis by using scanning electron microscopy had clarify the spent activated carbon already being regenerated using the chemical treatment. Therefore, chemical regeneration using hydrochloric acid solution can remove the pollutant from the spent activated carbon to be regenerated for further application.

1. Introduction
Activated carbon (AC) is a carbonization product of carbonaceous materials which utilizes the principle of adsorption to prevent environmental pollution. AC has been used for decades in industrials as adsorbent to remove impurities from gaseous or liquids and to polish effluent for meeting stringent discharge standards [1]. The adsorption performance of AC is determined by available surface area for physor-sorption and available adsorption site for chemisorption. Despite the fact that AC has excellent adsorption ability, the available surface area and adsorption sites are limited [2].

In industrial applications, AC requires to be replaced with fresh activated carbon (FAC) once the area and sites of AC were covered by adsorbate; in which the AC lost its adsorption capability and became spent activated carbon (SAC). The fate of SAC is either disposed of at landfill, regenerated or reused in industrial [3]. Regeneration of SAC refers to restoration of the available surface area and adsorption site on SAC or removal of adsorbate on SAC via desorption and/or decomposition. Many researches had studied on methods for carbon regeneration due to the fact that regeneration is cheaper than replacement of SAC. Furthermore, regeneration and reuse of SAC is also a practical way to reduce secondary pollution and conserve natural resources [4]. In Malaysia, the quantity of collected spent activated carbon in year 2012 is 1405.59 tons [5]. As one of the scheduled wastes, SAC must dispose of...
Carbon regeneration methods can be categorized into four major groups based on the mechanisms and agents involved in regeneration, namely thermal regeneration, chemical regeneration, microbiological regeneration and vacuum regeneration [7-8]. However, microbiological regeneration and vacuum regeneration are not feasible for industrial application as the former requires long regeneration time [9] and the latter is not well investigate on its regenerative performance [8]. Thermal regeneration methods such as thermal swing adsorption (TSA), steaming, electrothermal swing adsorption, microwave regeneration and gasification, involve heating process to desorb or degrade adsorbate on SAC [10-12]. On the other hand, chemical regeneration methods include regeneration with liquid water, NaOH, HCl and solvents, supercritical regeneration, electrochemical, AOP and pH changes [13-14].

Whilst many researchers have done extensive research and review on the carbon regeneration methods, solely thermal regeneration is used in industrial. Though thermal regeneration is the most practicable method in industrial, it is not an economically viable option due to high energy requirement and high volume of SAC is required to make it economically sensible [7]. Furthermore, thermal regeneration experiences carbon loss during the regeneration process. Comparing to thermal regeneration, chemical regeneration has a more attractive economic factor [3]. Chemically regenerated SAC experienced negligible carbon loss and could potentially improve adsorption capacity.

In this study, chemical regeneration method is used which involves treatment of the spent activated carbon by desorption process of adsorbates by the decomposition of adsorbed species using chemical agents such as acid to restore the adsorption capacity of activated carbon and hot water wash to increase the pores of the activated carbon. The benefits of chemical regeneration methods are that this treatment can be performed rapidly with no carbon attrition.

The objective of this research is to evaluate the adsorption capacity of regenerated spent activated carbon after desorption by chemical treatment and then develop a laboratory scale regeneration unit of spent activated carbon. At the end of the study, the regenerated spent activated carbon will be characterized based on its pore structure and surface morphology.

2. Materials and Method

2.1. Sample Preparation

The samples of spent activated carbon used by the wastewater treatment plant application in granular form were obtained from Meridian World Sdn. Bhd, which is one of the environmental service providing company at Sungai Petani, Kedah Darul Aman, Malaysia. The spent activated carbon were washed with plenty of water to remove impurities before drying it in oven at 105°C for 24 hours to remove the moisture contents.

The methylene blue and iodine solution were prepared for adsorption test where methylene blue number is to characterize the volume of mesopores of activated carbons while the iodine adsorption test for iodine number is used to characterize the activated carbons micropores quantity.

2.2. Activated Carbon Regeneration

In batch test, the spent activated carbon with HCl solution was added into 250 mL Erlenmeyer flask. Shaker machine was used to hold on the Erlenmeyer flask in order to shake well the content. The process was followed by a hot water wash and pH adjustment. Lastly, the carbon was dried in oven at temperature of 105°C for 24 hours to acquire a batch regenerated activated carbon.

In column test, the fixed bed column made of Pyrex glass with 1.2 cm inner diameter and 20 cm height will be used to pack the spent activated carbon inside the column to typify the laboratory scale regeneration unit by using the peristaltic pump for adjustment of the desired flow rate.
2.3. Activated Carbon Adsorption Test

In methylene blue adsorption test, an Erlenmeyer flask is used to enclose the regenerated carbon with methylene blue solution and contacted for 24 hours. The concentration of the treated methylene blue solution was determined by using U-2810 spectrophotometer uv/vis. Methylene Blue (MB) number is being expressed in term of the amount of methylene blue adsorbed ($q_e$).

$$MB\ number,\ q_{eq} \left(\frac{mg}{g}\right) = \frac{(C_0-C_e) \times V}{M}$$

where $C_0$ and $C_e$ are the initial and final concentration of methylene blue solution in mg/L respectively; $V$ is the volume of the treated solution in L; and $m$ is the dry mass of activated carbon in g.

The iodine adsorption test procedure was adopted based on the ASTM D4607-94 procedure [15]. The standard iodine solution will be in contact with the activated carbon sample. The remaining of iodine in the filtrate will be measured using titration method to obtain the volume of the 0.1 N sodium thiosulphate used.

3. Results and Discussion

3.1. Effect of concentration of HCl solution

The first set of experiments was designed for the regeneration of spent activated carbon using various concentrations of HCl solution. In the experiment, 1.0 g of spent activated carbon was allowed to contact with 50 mL of that are 0.01 M, 0.05 M, 0.1 M, 0.5 M, 1 M of HCl solution for 90 minutes. After obtained the regenerated carbon, the methylene blue adsorption test was conducted to obtain the methylene blue number of the activated carbon.

Figure 1 shows the influence of the concentration of HCl solution toward the methylene blue number. The higher the MB number, the more MB were adsorbed by the carbon, indicates higher regeneration efficiency. By using 0.05 M HCl solution can yield the highest methylene blue number compared to others which range from 0.01 M to 1 M. In this study, the concentration of 0.05 M HCl is most effective chemical regeneration condition for the spent activated carbon under optimum conditions to attain equilibrium concentration. However, this result has not been supported by the previous research that higher concentration of HCl especially 0.1 M HCl is selected as the tested concentration in their research [15]. There are several possible explanations for this result. A possible explanation for this might be that a higher concentration of HCl will deteriorate the spent activated carbon by diminishing heavy metal desorption. Although these results differ from some published studies, it is better by using 0.05 M HCl as the optimal value in this study since less concentration of HCl solution is required for economic consideration of regeneration purposes. The 0.05 M HCl solution concentration is selected as the tested contact time for the rest of the experimental studies.

![Figure 1. Concentration of HCl solution study](image-url)
3.2. Effect of Contact Time

The second set of experiments was conducted by using the same procedure as the first set of experiment but by using different various contact time that are 60 min, 90 min, 150 min, 240 min and 360 min respectively. Figure 2 shows the influence of the contact time toward the methylene blue number. The contact time of 360 minutes which equivalence to 6 hours is most effective chemical regeneration condition for the spent activated carbon. The higher the contact time, the higher the regeneration efficiency. A possible explanation for this might be that the longer duration of contact time can cause more surface of the spent activated carbon being in contact with the HCl solution for regeneration purposes. The contact time chosen for this study is not long enough to attain equilibrium. Equilibrium time need to be established for better desorption for economical purposes [15]. However, 6 hours is the allowable contact time for regeneration purposes since increase in time resulting higher treatment cost for operation. The contact time of 360 minutes is selected as the tested contact time for the rest of the experimental studies.

3.3. Effect of Volume of HCl Solution

The third set of experiment was designed for the regeneration of spent activated carbon using various volumes of HCl solution that are 10 mL, 20 mL, 30 mL, 40 mL and 50 mL respectively. The figure shows the influence of the volume of HCl solution toward the methylene blue number where the minimum volume that is 10 mL volume of HCl is most effective chemical regeneration condition for the spent activated carbon to yield the highest amount of methylene blue number. However, the findings of this batch three result do not supported by the previous research. It is because the significant improvement of the adsorption capacity should be the higher the volume of HCl the better for desorption to take place. It is somewhat surprising that only 10 mL volume of HCl was found to be the optimal condition for regeneration purposes. It is difficult to explain this result, but it might be affected by other factors that are not taken into consideration in this study such as the temperature of the HCl solution and activated carbon. The volume of 10 mL HCl solution is selected as the tested contact time for the rest of the experimental studies.

![Figure 2. Contact time study](image-url)
Figure 3. Influence of volume of HCl used

3.4. Effect of Flow rate in Column Test

There is a demand to use column type operation which widely used in practice since the data obtained from batch test are commonly not suitable for most of the treatment system. Thus, it is crucial to study the regeneration process based on the column test. The effect of the flow rate on the regeneration of spent activated carbon was investigated by varying the flow rate that are from 0.1 mL/min, 0.5 mL/min, 1 mL/min, 2 mL/min, 3 mL/min, 4 mL/min and 5 mL/min respectively with a constant mass of spent activated carbon of 5 g. The optimal regeneration conditions which combine the batch one, 0.1 M HCl, batch two, 360 minutes and batch three, ratio of 1g to 10 mL that is in this column test, 50 mL of HCl is used for 5 g of spent activated carbon were implemented in the column test. The best chemical regeneration conditions based on vary of flow rate was 1 mL/min. The increase in the flow causes a reduction of the contact between the HCl solutions with the spent activated carbon that causes a fall in the kinetics of desorption. The HCl solutions will have insufficient residence time to penetrate and diffuse deeply into the pores of the spent activated carbon for desorption purposes when the flow rate is high. However, this condition only favorable only until one value of the flow that a drop in the flow beyond this value, localized in this conditions towards less than 1 mL/min will cause a fall in the desorption efficiency since the flow rate is too small for the overall contact due to between the HCl solutions with the spent activated carbon.

Figure 4. Flow rate study

3.5. Methylene Blue Adsorption Test

The experimental results of the methylene blue number for the spent activated carbon, batch regenerated activated carbon and column regenerated activated carbon were shown. The higher the methylene blue number indicates the higher the activated carbon adsorption capacity since can adsorb more methylene blue dye into the macropores of activated carbon. Figure 5 presents the experimental data of methylene blue number for the comparison between different types of activated carbon. The methylene blue
number of spent activated carbon, batch regenerated activated carbon and column regenerated activated carbon are 8 mg/g, 40 mg/g and 38 mg/g respectively. The chemical regeneration of the spent activated carbon using HCl solution has almost same regeneration capacity for the batch regenerated activated carbon and column regenerated activated carbon for the increment of mesopores according to the methylene blue test. The methylene blue number of different types of carbon shown the trend of carbon as: Batch regenerated activated carbon (BRAC) > Column regenerated activated carbon > (CRAC) > Spent activated carbon (SAC). The methylene blue number normally ranges from 200 mg/g to 400 mg/g. The result of this study is quite low since by using the chemical regeneration will have incomplete regeneration as if the adsorption is chemical adsorption where chemical bond was formed, it is quite difficult to break the bond by only using the chemical treatment. Besides, the spent activated carbon from the wastewater treatment applications contains a heterogeneous mixture of contaminants that will cause difficulties to be regenerated.

![Figure 5. Methylene Blue Number of Different Types of Carbon](image)

3.6. Iodine Adsorption Test
The iodine adsorption test was conducted for the spent activated carbon, batch regenerated activated carbon and column regenerated activated carbon. The iodine number for the activated carbon were obtained from the graph of Least Square Fit. The Least Square Fit graph based on the Iodine adsorbed (X/M) versus Iodine Residual (C) to find out the iodine number of the respective activated carbon. The higher the iodine number indicates the higher the activated carbon adsorption capacity since can adsorb more iodine into the micropores of activated carbon. Figure 6 presents the results by comparison for the iodine number of different types of carbon. The iodine number of spent activated carbon, batch regenerated activated carbon and column regenerated activated carbon are 92 mg I/g, 120 mg I/g and 174 mg I/g respectively. The iodine number of different types of carbon shown the trend of carbon as: Column regenerated activated carbon (CRAC) > Batch regenerated activated carbon > (BRAC) > Spent activated carbon (SAC). These trend were different compared with the trend of the methylene blue number of the activated carbons. It could be due to the chemical regeneration using HCl is more efficient to regenerate the micropores of the spent activated carbon compared to the mesopores by using the methylene blue test. The result of the iodine number after regeneration is still quite low compared to the commercial activated carbon where the typical range of iodine number are 500 - 1200 mg/g [16]. This may be due to the contaminant already form bonds especially chemical bond on the spent activated carbon and the spent activated carbon consists of a mixture of the compound where multiple regenerants are required.
3.7. Characterization of Adsorbent
Scanning electron microscopy (SEM) of the surface morphology of three samples that were spent activated carbon, batch regenerated activated carbon and column regenerated activated carbon were observed. The micrograph of Fig. 7 (A) showed the original pores of the spent activated carbon with the presence of mesopores and micropores. There is less amount of micropore with distorted mesopore structure that were imaged. It can be seen there were lighter coloured deposits on the surface of the spent activated carbon which most probably is the pollutant or contaminant which had been adsorbed by the spent activated carbon. Fig.7 (B) showed that there are different size and shapes of pores with larger amount of micropores could be observed in surface of batch regenerated activated carbon compare with spent activated carbon. There can be seen that less amount of pollutant or contaminant that present on the surface of the batch regenerated activated carbon. Fig. 7 (C) showed that there are obvious structural change that are bigger size and rigid micropore structure of the column regenerated activated carbon could be seen from the plate. The presence of micropores in the column regenerated activated carbon was supported by the findings from the iodine adsorption test. The iodine number which indicates micropores for the column regenerated activated carbon are higher compared to the batch regenerated activated carbon. The micrographs clearly shown the higher amount with bigger diameter of micropores of the column regenerated activated carbon as compared with the batch regenerated activated carbon. These results indicated that acid treatment plays an important role for increment of the micropores surface area and volume.

![Figure 7. SEM images of (A) Spent Activated Carbon, (B) Batch Regenerated Activated Carbon and (C) Column Regenerated Activated Carbon](image)

4. Conclusion
In conclusion, the optimal regeneration condition is 0.05 M HCl with a contact time of 360 minutes with 10 mL volume of HCl solution. The effect of the flow rate supplied to the column was studied that the
most effective chemical regeneration for column test is using the flow rate of 1 mL/min. From the experimental information gathered, it can be shown that the methylene blue number of different types of carbon shown the trend as BRAC > CRAC > SAC that the mesopores of the BRAC is the highest while the iodine number of different types of carbon shown the trend as CRAC > BRAC > SAC that the micropores of the CRAC is the highest as can be seen from the SEM result as well. This study has revealed that chemical regeneration has fairly removed some of the adsorbed contaminants of concern such as heavy metal from the surface of the pores of spent activated carbon. Chemical regeneration using HCl solution can remove the pollutant from the spent activated carbon from industrial wastewater application to be regenerated for further application. Therefore, the effectiveness of chemical regeneration of spent activated carbon which is only partially effective has been established. It may be concluded that adsorptive properties were improved slightly during regeneration of the spent activated carbon.

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