CHAPTER 6

GENERAL DISCUSSION AND CONCLUSION

6.1 Conclusions of the Thesis

The batch adsorption was conducted using activated carbon of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark for the removal of heavy metals, and methylene blue. The important outcomes of this experiment are mentioned below. The batch adsorption techniques depend on some important factors such as adsorbent dose, contact time, initial concentration, pH etc for removing pollutants from wastewater. This study concludes that the major findings with regard to the objectives are summarized. The strengths and limitations of this thesis are also described.

6.2 The Used of Agricultural Waste Convert into Activated Carbon

There are some techniques to eliminate toxic metals and dyes from wastewater. Adsorption is one of the best methods for purifying spiked aqueous solution. In this study, the five cheap naturally adsorbents such as rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark were used to define their effectiveness for reducing contaminants from spiked aqueous solution. Agricultural by-products and their wastes offer an inexpensive and abundant source of activated carbons but it has a disposal problem. The conversion of agricultural waste into activated carbons would offer significant economic value to the community, overcome the waste disposal issues.

The chemical activation process has more advantages than physical activation. The chemical activation can produce mesoporous activated carbon with a larger surface area. Usually, the activating agent used is basic salts and bases. A more nonthreatening chemical is preferred as an activating agent. Hence, $ZnCl_2$ is chosen as it is not a hazardous chemical and not harmful. Impregnation with $ZnCl_2$ is a simple process but offers a highly porous carbon structure. Ash in activated carbon is an impurity in the carbonaceous material. Ash consists of minerals such as silica (Si), aluminum (Al), iron (Fe), magnesium (Mg) and calcium (Ca). These minerals will compete for the adsorption sites with adsorbates during the adsorption process. The ash can fill and block the existing pores that results in a decrease in the surface area. Ash can be removed using the demineralization process. The demineralization process involves the dissolution of minerals and metals into acid or alkali solutions such as hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4) or NaOH. This process is called de-ash treatment, where hydrochloric acid was used to dissolve the minerals. So, it is necessary to use those waste for solving environmental problems. The natural waste was converted into adsorbents successfully which gained 439.23 m^2/g of surface area including the micropore (396.93 m^2/g) for the best activated carbon of *Moringa oleifera* bark. The result indicated the effectiveness of the activating agent used ($ZnCl_2$ and H_2SO_4) and the temperature applied during the process. The development of microporous structure can be improved during the carbonization temperature (700 °C). The applied temperature helped to eliminate disorganised matter in the carbon to improve pore structure. The surface areas were also increased due to the application of acid during the demineralization and activation process.

6.3 Evaluation of the Prepared Adsorbents in Batch

Batch equilibrium studies and column studies were conducted using three different adsorbates such as heavy metals (lead, nickel, copper, and cadmium), dye (methylene blue) to determine the efficiency of the prepared activated carbon in adsorption process. There were four important factors on the adsorption uptake such as adsorbent dose, initial adsorbate concentration, contact time, and solution pH.

Increasing the adsorbent dosage, the uptake of heavy metals and methylene blue from an aqueous solution also was increased. It was reached equilibrium position in 0.025 g/100 mL solution. The uptake of metal ions was improved in the adsorption process with a growing quantity of adsorbents. It can be occurred due to having more active sites of activated carbon due to adsorption. We can observe that further increasing the dose but metal-binding quantity was not increased significantly. It can be happened due to reaching an equilibrium state of both bound to the activated carbon and unadsorbed contaminant in solution.

It was proven that adsorption uptake was increased when initial concentration increased from lower concentration (5 mg/L) to higher concentration (50 mg/L). Initial concentration offered the driving force to overcome resistance during mass transfer between the liquid and solid phase. Therefore, once the driving force increased, the mass transfer was increased.

Another important parameter was the contact time for the interaction between the adsorbents and the adsorbates. The quantity of adsorbate adsorbed at time, q_t was increased when the contact time increased. From that result it was observed that the adsorption capacity of the metal ions by adsorbents was good within 10 minutes for rice husk, coconut coir, and *Moringa oleifera* bark due to a large number of surface sites available for the adsorbates molecules at the initial stage but after 10 minutes occurred some desorption of nickel and cadmium then uptake metal ion adsorption increases with time up to 1 hour. On the other hand, the adsorption capacity of methylene blue was slightly increased from 10 minutes to 180 minutes with steady. However, after some time, the presence of repulsion between the solute molecules of the solid and bulk phases caused some resistance for the remaining surface sites to be filled, and the adsorption was slowing up.

The adsorption of all heavy metals and methylene blue were increased with increasing pH from 2 to 6 then dropped. The optimum pH value for lead, nickel, copper, cadmium, and methylene blue was at pH 6. At lower pH, the adsorption capacity was unfavourable for all metal solutions and dye by all activated carbon. With the increasing pH value, the concentration of H^+ ion in solution decreases, the negative surface charge will be an increase on the activated carbon above the point of zero charge pH (pzc), the pH (pzc) for the prepared five activated carbon was found to be around (4.1-5.4). For this reason, to attract metal cations and methylene blue mostly in positive form M^{2+} (Pb^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and MB^+) and its simply can be adsorbed onto adsorbents. If pH is above 6, the decrease in metal adsorption can occur for three factors. First, with increasing the pH value, the negatively charged on adsorbent surface also increased. However, at the same time metal was changed from a molecular state to an ionic state. That was significant for the repulsion force between metal ions and the activated carbon. Second, the presence of a repulsion force between the metal ions which were adsorbed by the activated carbon. Third, the negative charges on the activated carbon's surface were repulsive that blocked the disaggregation of metal ions and metal adsorption.

6.4 Efficiency of the Prepared Adsorbents on Removal of Heavy Metals

The prepared activated carbon was proven to be effective in removal of adsorbates such as lead, nickel, copper, and cadmium from spiked water solution. From the studies, the experimental q_{max} for rice husk are found to be 27.17, 20.45, and 12.52 mg/g, coconut coir are 28.49, 20.88, and 54.95 mg/g, corn cobs are 27.4, 13.3, 15.55 mg/g, neem bark are 27.1, 9.38, and 3.38 mg/g, and *Moringa oleifera* bark are 27.86, 20.43, and 17.01 mg/g for three metals which are Ni, Cu and Cd ions that are comparable with theoretically calculated q_{max}. This study observed that the adsorption percentage of lead (II) was higher (100 %) than other metals (nickel, copper, and cadmium). This is due to increases of adsorption by ion exchange with increasing ion radius. Here the ion radius of Pb^{2+} is higher than Cu^{2+} and Ni^{2+}. Moreover, lead can easily form complexes with oxygen functional groups of adsorbents. However, the adsorptive amount of Pb (II) was higher than those of metal (II). The M (II) uptake on activated carbon may be also described by ion exchange process. The major functional groups of adsorbents are the carboxyl, hydroxyl, aromatic (C=C) group which can participate in the ion exchange process.

6.5 Efficiency of the Prepared Adsorbents on Removal of Methylene Blue

The removal of methylene blue was good using prepared all activated carbon. From the graph, it can be observed that with increasing the adsorbent dosage, the removal of methylene blue also was increased. The removal percentage of methylene blue were 94.60 %, 99.40 %, 99.90 % 100 %, and 94.20 % using 0.025 g of adsorbents of the activated carbon of rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively. There is a far difference for q_e values of the first order equation between experimental values (108.94, 107.71, 107.71, 109.34, and 108.12 mg/g) and calculative values (8.34, 7.62, 8.01, 5.59, and 4.54 mg/g) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark respectively. The coefficient regression value (R^2) was not close to 1. So, these graphs were not fitted with the first-order model. On the other hand, the experimental value (q_{exp} ~ 108.94, 107.71, 107.71, 109.34, and 108.12 mg/g) and calculative values (q_{cal} ~ 111.10, 108.69, 108.69, 111.10, and 108.69 mg/g) for rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark, respectively were closed for the pseudo-second-order model and also coefficient regression constant (R^2) was almost equal to unity (~1) for all activated carbon. So, the adsorption of methylene blue kinetics parameter for all activated carbon was well fitted to the second order model.

6.6 Conclusion

Some important findings from this study are shown below:

1) Agricultural wastes such as rice husk, coconut coir, corn cobs, neem bark, and *Moringa oleifera* bark were successfully used for production of activated carbon as precursor using chemical activation methods. Its adsorbent properties were inexpensive, availability, profitability easy to process, effectiveness in reducing the concentration of heavy metal ions (Pb, Ni, Cu, Cd), and methylene blue to very low levels.
2) The carbonization temperature and chemicals with char impregnation ratio were vital factors for improving the adsorption performance of the activated carbon. The optimum conditions were obtained from chemicals ($ZnCl_2$+ H_2SO_4) with char impregnation ratio (5:1) and carbonization temperature (700 °C) for producing the best activated carbon from the *Moringa oleifera* bark precursor.
3) The surface area of produced adsorbents was relatively high (439.18 m^2/g) with average pore diameters (17.23 A^0). FTIR analyses indicated the presence

of functional groups such as hydroxyl (O-H), carboxyl (C-O) and aromatic (C-H & C=C) on the surface of adsorbent. The adsorbent was characterized by BET surface morphology and SEM images analysis. The SEM images showed all pores of activated carbon were filled-up with heavy metals after the adsorption process.

4) Batch studies removal efficiency depends on the vital variables such as adsorbent dose, contact time, initial concentration, pH etc. The adsorption process is pH dependent. At pH 6, lead was absolutely (100%) removed from spiked aqueous solution using all activated carbon and copper (99%), nickel (88.10%), and cadmium (69.40%) also significantly was reduced using *Moringa oleifera* bark from aqueous solution. The Freundlich isotherm model ($R^2 \approx 1$) was well fitted with experimental data than the Langmuir and Dubinin Radushcavick model.
5) Methylene blue was the maximum reduction (~100%) in lower concentration at pH 6 using activated carbon of neem bark and methylene blue was reduced more than (95 %) using other activated carbon. A second-order kinetic model with a regression correlation factor ($R^2 \approx 1$) was a good result and preferred in contrast to the first order model.
6) *Moringa oleifera* bark, rice husk and coconut coir were shown better efficiency for reducing heavy metals than corn cobs and neem bark but corn cobs and neem bark was better for reducing methylene blue than others. The activated carbon of *Moringa oleifera* bark was shown to have the best removal activity from wastewater for all heavy metals, and methylene blue.

6.7 Scope for Future Research

Those activated carbon can be used to purify the real industrial wastewater for practical applications. Adsorbent regeneration system and proper discarding systems of agricultural waste may be developed. Pre-treatment process of precursor may be developed with a more cost-effective process for improving adsorption capacity of activated carbon.