Adsorption of 4-Nitrophenol from wastewater using Sea Mango (Cerbera odollam) based Activated Carbon

Nurul Zufarhana Zulkurnai, Nor Wahidatul Azura Zainon Najib*, Umi Fazara Md Ali, Tan Ru Shien
School of Environmental Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Perlis, Malaysia
*e-mail: norwahidatul@unimap.edu.my

Abstract. The presence of phenols and phenolic compounds in water and wastewater has gained great public attention and it is one of the most frequent pollutants in wastewater. In this study, the adsorption of 4-Nitrophenol from wastewater using activated carbon prepared from the non-edible Sea Mango (Cerbera odollam) fruit was investigated. The Sea Mango Activated Carbon (SMAC) was prepared through a physicochemical activation which consists of H3PO4 impregnation and followed by CO2 gasification. The influences of process variables represented by solution pH value, contact time, initial concentration and adsorbent dosage on removal efficiency of 4-NP onto Sea Mango Raw Material (SMRM) and Sea Mango Activated Carbon (SMAC) were studied. Result showed that the optimum pH for 4-NP removal was at pH 3. The dosage usage required to complete 100 ml of 4-NP on SMRM and SMAC was 1.0 g. Batch studies were performed to evaluate the adsorption process, and it was found that the Freundlich isotherm effectively fits the experimental data for the adsorbates better than the Langmuir model with the highest adsorption capacity 158.730 mg/g of 4-nitrophenol on SMAC. It was found that 70.49% and 97.98% of 4-NP was adsorbed onto SMRM and SMAC, respectively, at an initial concentration of 20 mg/L.

Keywords: Activated carbon; Sea mango (Cerbera odollam); Adsorption; 4-Nitrophenol

1 Introduction

Nitrophenol usually formed because of pesticide contamination and phenol image has considerable solubility in water. In order to reduce this problem, various regulatory agencies have to set a limit for the concentration of phenolic compounds in industrial effluent before it can be safely discharged to water bodies and in Malaysia, the concentration should not surpass 10 mg/L. Adsorption was found to be an excellent choice and takes precedence over other techniques for water re-use for low initial cost, simplicity of design, convenient operation and insensitive to toxic substances [1].

Water pollution by heavy metal is regarded as a serious environmental problem due to their toxicity, long persistence, bioaccumulation and biomagnifications [2]. 4-Nitrophenol (4-NP) is considered as the hazardous metal found in wastewater of several industries. In this study, 4-NP is used as the model adsorbate, since it has been suggested as representative of aqueous organic pollutants.

Activated carbons are broadly used as efficient and versatile adsorbents for purification of water, air and many chemicals and natural products. Water treatment is by far, the largest outlet for activated carbon [3]. Various carbonaceous materials, such as coal, lignite, coconut shell, wood and peat are used in the production of commercial activated carbon [4].

Adsorption process by using activated carbon is an effective and reliable method in eliminating impurities in wastewater. It has been reported to have relatively large surface area per unit volume and submicroscopic pores in which adsorption takes place [1]. Adsorption of 4-Nitrophenols from the wastewater occur as a result of molecule which exert attractive force especially molecules at the surface of activated carbon.

The efficiency of activated carbon largely depends on the source and preparation conditions. Furthermore, agricultural wastes offer the most available and cheapest of all the known raw materials.
The production of activated carbon from an abundant carbonaceous material is a relatively low-cost alternative adsorbent. In this research, the adsorption of 4-Nitrophenol from wastewater using activated carbon prepared from the non-edible Sea Mango (*Cerbera odollam*) fruit was investigated.

2 Material and methods

2.1 Activated Carbon Preparation
Sea mango (*Cerbera odollam*) acted as precursory material for AC was collected along the road side of School of Environmental Engineering in Perlis. The skin and seed of sea mango were removed from its fibrous shell and subsequently, washed it to get rid of any dirt. The cleaned fibrous shell was then dried in an oven at 105 °C for a total hour of 24 h. The dried fibrous shell was ground and sieved into a particle sizes ranging from 1 to 2 mm.

The precursor was then semi-carbonized at 200 °C for 0.5 h in inert atmosphere with the presence of continuous flow, 1.5 L/min of nitrogen gas. A certain weight of dried fibrous shell was impregnated with different concentration of 53.75 % H$_3$PO$_4$ solution at impregnated ratio 2:1 of H$_3$PO$_4$ to the dried fibrous shell. The mixing was conducted at room temperature for 4 h to provide the well penetration of H$_3$PO$_4$ into the fibrous shell. Then, the impregnated fibrous shell was dried in an oven at 110 °C.

The impregnated fibrous shell was then heated to carbonization temperature of 519.8 °C in the tubular furnace in the present of carbon dioxide gas for 2.3 h activation time. This optimized method of preparing SMAC samples is similar to that of recently published by Md Ali et al., 2018 [5]. The carbonized product was repeatedly washed with hot distilled water to remove the excess H$_3$PO$_4$. The prepared SMAC was then dried in an oven at 110 °C for 2 h. Finally, the SMAC was grinded and sieved into 300 – 600 μm.

2.2 Preparation of adsorbate
4-Nitrophenols was weighted with weighing scale. 1000mL of the stock solution was prepared by dissolving 1 g of 4-NP in the 1000 ml of distilled water. The desirable experimental concentration of solution was prepared by diluting the stock solution with distilled water when necessary.

2.3 Characterization of adsorbent
The surface area of the activated carbon was determined using a BELSORP-Mini machine. Surface morphology and element composition analyses were conducted using a scanning electron microscope (SEM), and the total ash content of the adsorbent was evaluated in accordance with ASTM standard D2866 – 11 (ASTM, 2011).

2.4 Batch Adsorption of 4-Nitrophenol (4-NP)
Stock solution was prepared by using 1 g of 4-NP and dissolve in the 1000 mL of distilled water to obtain adsorbate solution of various initial concentrations.

The effect of pH, contact time and adsorbent dosage were studied using 20 mg/L 4-nitrophenol. The effects of adsorbent dosage of SMRM and SMAC were conducted by contacting time and initial concentration of 20 mg/L of 4-NP of with varying quantities of adsorbent dosage (0.2 to 1.0 g) in a series of 25 mL Pyrex conical flasks at a neutral pH.

The effect of initial concentration of 4-NP was studied using different initial concentrations (20, 40, 60, 80 and 100 mg/L) with 1 g of SMRM and SMAC, stirred at 200 rpm for 3 h. The concentration changes of the individual compounds in the solutions were determined by UV-VIS spectrophotometry. The maximum absorbances for each solute from the highest standard solution prepared were found using scanning spectrophotometry at the respective wavelength maxima, λ. The λ applied were 318 nm for 4-NP. The calibration plot of absorbance vs. concentration for all the standards showed a linear working range with correlation coefficient ≥ 0.99.
3 Result and discussion

3.1 Characterization Result

3.1.1 BET surface area and ash content
BET is an alternative method to determine the surface area of activated carbon. The value of the activated carbon BET on SMAC test was 857.93 m²/g. The value of ash content test for SMAC was 8.7%.

3.1.2 Surface Morphology
Surface morphology represents the physical structure of each sample as shown in Figure 1 (i)-(ii). SMRM and SMAC surface photographs are shown in Figure 1 (i). Magnification by SEM of 300x and 100x is made to show the morphology of the surfaces on SMRM and SMAC. It can be seen that the SMRM are not clearly seen by the observation of the size of the pore. After the impregnation by H₃PO₄ and activation process, the pore size of the SMAC is obviously bigger compared to the SMRM as shown in Figure 1 (ii). The well develop pores will increase the surface area of the activated carbon and at the same time will increase the adsorption capacity of the adsorbate [6].

(i) SMRM (magnification 300x)  (ii) SMAC (magnification 100x)

Figure 1 SEM image for (i) SMRM and (ii) SMAC.

3.2 Effect of Adsorbent Dosage on Adsorption
Figure 2 indicates the percentage removal of 4-Nitrophenol increased correspondingly with the increased of the adsorbent dosage, from 15.91% to 30.88% removal of 0.2 g to 1.0 g adsorbent dosage respectively for SMRM. While for SMAC, the percentage removal of 4-nitrophenol increased correspondingly with the increased of the adsorbent dosage, from 87.48% to 91.49% removal of 0.2 g to 1.0 g of adsorbent dosage respectively for SMAC.
The expanding surface area or tying sites, where the adsorption takes place with the expanding of AC dosage, are demonstrated by the increasing of the efficiency for the SMRM and SMAC dosage. At the adsorbent dosage of 0.6 g until 1.0 g, the removal efficiency started to reach a constant value which is 91.49% removal at 1.0 g for SMAC. Therefore, 1.0 g of adsorbent dosage was used for further study with 100 mL of 4-NP simulated solution. The result obtained is similar to the test conducted by Asrar [7]. The same amount of adsorbent dosage will be used for SMRM.

3.3 Effect of Solution pH on Adsorption

The pH of solutions is also one of the parameters which effect the removal of 4-NP from the aqueous solution by adsorption process. The adsorption of 4-nitrophenol onto SMRM and SMAC is determined by the effect of variation of the initial solutions pH (3, 5, 7, 9).

Figure 2. The removal efficiency on the adsorbent dosage of SMRM and SMAC

![Figure 2. The removal efficiency on the adsorbent dosage of SMRM and SMAC](image)

Figure 3 illustrates the suitable dosage chosen at given dosage of 1.0 g per 100mL of 20 ppm of 4-NP at room temperature and 180 minutes time shaking with 200 rpm. For 4-NP, the adsorption removal percentage decreases with an increase in pH from 3 to 5 and from 3 to 7 for SMRM and SMAC respectively. Figure 3 also shows that 32% maximum removal percentage of SMRM is
achieved at pH value of 3. While for SMAC, a maximum removal percentage of 92% is obtained at pH of 3. Therefore, the values of 3 are considered to be the best pH for removal of SMRM and SMAC from 4-NP, respectively. This is coherent with result reported by Asrar [7].

3.4 Effect of Initial Concentration and Contact time on Adsorption

Figures 4 and 5 represent the results for the effect of initial concentration and contact time on the removal of 4-NP from aqueous solution at an initial concentration of 20 mg/L.

![Graph showing the effect of initial concentration on removal efficiency of SMRM.](image_url)

**Figure 4.** Effect of the removal efficiency on different concentration and contact time of SMRM

![Graph showing the effect of initial concentration on removal efficiency of SMAC.](image_url)

**Figure 5.** Effect of the removal efficiency on different concentration and contact time of SMAC

The effect of initial concentration of 4-nitrophenol was studied using different initial concentrations (20, 40, 60, 80, and 100 mg/L) with 1.0 g of each SMRM and SMAC, stirred at 200 rpm for each chosen minute (15, 30, 60, 90, 150 and 180 minutes). Increasing initial concentration 4-nitrophenol increasing the removal efficiency as the minutes is increasing. This can be due to the absence of
adsorption sites for the extra molecules at a constant amount of the adsorbent, while for the adsorption of 4-NP, which have smaller radius, it slightly different is high for all concentrations.

It can be seen that the amount of all the adsorbents adsorbed onto SMRM and SMAC increases with time and about 70.49% and 97.58% of 4-NP respectively had been removed within the first 15 min of agitation. The time profile for adsorbents is a single, smooth, and continuous curve leading to saturation, which suggests possible monolayer coverage of the adsorbents on the surface of the SMRM and SMAC [3].

3.5 Sorption Capacity of 4-Nitrophenol
The sorption capacity of 4-NP was calculated by using Eq. 1.

\[ q_e = \frac{V(C_0 - C_f)}{m} \tag{1} \]

Whereby, \( V \) is the volume of 4-NP, \( C_0 \) and \( C_f \) is the initial and final concentration of 4-NP and \( m \) is mass of adsorbent. The results were presented in Figure 6. It can be seen that the amount of sorption capacity increases correspondingly with time. For the first 15 minutes, the amount of sorption of 20 ppm, 40 ppm, 60 ppm, 80 ppm, and 100 ppm were 0.1390 mg/g, 1.3582 mg/g, 2.3175 mg/g, 3.4099 mg/g and 4.2772 mg/g for SMRM respectively. For 180 minutes, the amount of sorption increases to 0.7660 mg/g, 1.8143 mg/g, 3.3403 mg/g, 5.0931 mg/g and 7.0488 mg/g, for SMRM respectively.

In addition, for the SMAC, the first 15 minutes, the amount of sorption of 20 ppm, 40 ppm, 60 ppm, 80 ppm, and 100 ppm were 1.7734 mg/g, 3.7509 mg/g, 5.7469 mg/g, 7.7294 mg/g and 9.7 mg/g, respectively. For 180 minutes, the amount of sorption increases to 1.8509 3.8357 mg/g, 5.8123 mg/g, 7.7736 mg/g, 9.7576 mg/g and mg/g, respectively.

![Figure 6. Sorption capacity of 4-NP at difference concentration and time for SMRM](image-url)
Figure 7. Sorption capacity of 4-NP at different concentration and time for SMAC

The graph obtained in Figure 7 shows the single, smooth and continuous curves towards saturation. This indicates the coverage of monolayer formation of 4-NP molecule on SMRM and SMAC surface [8].

3.6 Adsorption Isotherm Study

3.6.1 Langmuir Isotherm

Figure 8. Langmuir isotherm of 4-Nitrophenol on the SMRM
Figures 8 and 9 show the Langmuir graph isotherm for 4-NP adsorption onto SMRM and SMAC at different concentration. The $q_m$ value was 6.6269 mg/g and 158.730 mg/g which indicates the area occupied by a monolayer of sorbent, $K_L$ was 1.0258 L/mg and 0.1435 L/mg indicates favourable adsorption process for SMRM and SMAC, respectively. $R_L$ was 0.962 and 0.767 for SMRM and SMAC, respectively which shows that Langmuir isotherm model was the best fit for SMRM. Other parameters in Langmuir isotherm parameter were $R_L$ which could be express by dimension constant.

From the calculation, the value of $R_L$ for 20 ppm, 40 ppm, 60 ppm, 80 ppm, and 100 ppm were 0.0465, 0.0238, 0.0159, 0.0120, and 0.0097 for SMRM and 0.2584, 0.1484, 0.1041, 0.0801 and 0.00651 for SMAC, respectively. The values of $R_L$ calculated were found to be within 0 and 1 for SMRM and SMAC. These prove that the adsorption of 4-NP is favourable by using both adsorbents and the monolayer coverage of 4-NP at the outer space.

3.6.2 Freundlich Isotherm

Figures 10. Freundlich isotherm of 4-Nitrophenol on the SMRM
Figures 11. Freundlich isotherm of 4-Nitrophenol on the SMAC

The Freundlich model is an empirical equation which is based on the assumption that there are heterogeneous adsorptive energies on the surface of the adsorbent. The value of $K_F$ was 0.0284 and 2.9188 for SMRM and SMAC, respectively. It is an indicator of adsorption capacity gained from the intercept of the graph from Figures 10 and 11. The $n$ value was 0.5433 and 2.4823 for SMRM and SMAC, respectively. This indicates the adsorption of 4-NP is favourable by using SMAC due to the $n$ value is greater than 1 [9]. The $R^2$ value was 0.9137 and 0.9156 for SMRM and SMAC, respectively. The results for both isotherms were tabulated in Table 1 which highlights that Freundlich isotherm is the best fit isotherm for SMAC according to $R^2$ values.

Table 1. Parameters of Langmuir and Freundlich Isotherm Models for 4-Nitrophenol Adsorption

| Sample | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ | $n$ | $R^2$ |
|--------|--------------|--------------|-------|-------|-----|-------|
| SMRM   | 6.6269       | 1.0258       | 0.962 | 0.0284| 0.5433| 0.9137|
| SMAC   | 158.7300     | 0.1435       | 0.767 | 2.9188| 2.4823| 0.9156|

4 Conclusions

Removal efficiency of 4-NP increase as the amount of adsorbent dosage and contact time increased whilst decrease as the initial concentration of adsorbate increased. The ideal $pH$ for 4-NP removal is at $pH$ 3 while the lowest removal efficiency is at $pH$ 9. Langmuir isotherm well represent the equilibrium data of adsorption of 4-NP onto SMRM, whilst, Freundlich isotherm is the best fit isotherm for the equilibrium data of 4-NP adsorption onto SMAC.

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