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A Preliminary Study on the Potential Dye Adsorbance by Activated *Meretrix lamarckii* (*M. lamarckii*) Shells

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Abstract. Dyestuff manufacturing and consuming industry have led to water pollution through their discharge of untreated wastewater. Presence of dye pigments in water bodies may cause carcinogenic, mutagenic effects and caused harm to the entire aquatic ecosystem. This research has carried out to examine the adsorption potential of treated *Meretrix lamarckii* (*M. lamarckii*) shells towards Malachite Green (MG) dye removal. Activation with hydrochloric acid (HCl) and potassium hydroxide (KOH) was used for the conversion of seashells into TS1 and TS2 respectively. Following that, batch adsorption studies were carried out at 30°C using TS1 and TS2 to study the effect of contact time, pH, initial concentration of adsorbate and adsorbent dosage on dye removal percentage. The optimized contact time for TS1 was 210 minutes, with the best performance in pH 10 aqueous medium, 10 mg/L initial concentration of MG and optimum dosage of 1.0 g. Whereas for TS2, the optimized contact time was shorter than TS1, which was only 90 minutes to attain equilibrium state. The optimized pH and initial concentration of adsorbate were the same as TS1. While optimized adsorbent dosage for TS2 was lower than that of TS1, which was 0.8 g. Based on the results obtained, TS2 was found to be more effective in MG dye removal than TS1. High efficiency of TS2 was due to the presence of alkyl halide group and its larger total surface area. From the study, it can be concluded that treated *M. lamarckii* possesses high adsorption efficiency and potential to become a new introduce adsorbent in wastewater treatment technology.

1. Introduction

Dyestuff manufacturing and consuming industry have led to water pollution when untreated coloured wastewaters directly discharge into water bodies [1]. Presence of excessive dyes in water bodies will block the penetration of sunlight and reduce the photosynthesis rate of phytoplankton and algae, thus, affect the whole aquatic ecosystem [2]. The dye molecules and their metabolic products can lead to serious human health problems as they bring toxic, mutagenic and carcinogenic effects [3].

Most dyes are made up of aromatic molecular structures which made them very stable and non-biodegradable in nature. Hence, some conventional wastewater treatment methods such as coagulation or flocculation, ozonation, chemical oxidation and electrochemical treatment that have been used in some industries today are not suitable for dye removal [4]. Currently, many researches have been done on the potential dyes adsorbance by activated carbon prepared from many types of raw material. Activated carbon appeared to be the most suitable and effective method in dye removal for its high porous structure [5].



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Seashell waste that normally disposed at landfill site will cause environmental problems such as bad odours, air pollution and soil pollution [6]. In this study, *M. lamarckii* shells were chosen as raw material of adsorption for malachite green (MG) removal due to low cost, abundance and easily available especially at the coastal area and seafood restaurant [7]. The sea shells were activated using hydrochloric acid (HCl) and Potassium Hydroxide (KOH). The effect of contact time, initial pH, initial concentration and adsorbent dosage were studied and compared between the two activation processes on the highest capacity of the dyes adsorptions.

2. Methodology

2.1 Sampling

M.lamarckii shells were collected from local stalls at Tanah Merah, Kelantan and transported to the laboratory immediately after the sampling. The shells were washed with tap water to remove any dirt and unwanted material such as tissue attached to *M.lamarckii* shells. Then, the shells were rinsed with distilled water and dried overnight at room temperature. Dried shells were crushed using mortar and pestle and later sieved with 250 μm sieves. The dried samples were then being kept in zipper bag at room temperature before further analysis.

2.2 *M. lamarckii* Shells Acid Activation (TS1)

About 200 g of *M.lamarckii* shell powder was carbonized at 700°C for 2 hours in a furnace. Then, the samples were allowed to cool down to room temperature before mixed with 250 mL of 5.5 M hydrochloric acid (HCl). The mixture was then boiled for 2 hours at 350°C on a hotplate. After the slurry had cooled, it was filtered, washed and rinsed using distilled water until the residual liquid became pH 7 to remove all the acid residues. The acid activated shells powder (TS1) was dried again in an oven at 110°C for 3 hours. Then, the TS1 powders were kept in zipper bag for further experiments.

2.3 *M. lamarckii* Shells Alkali Activation (TS2)

About 200 g of *M.lamarckii* shell powder was first incinerated at 700°C for 1 hour under constant nitrogen flow inside a tube furnace. After that, it was soaked in potassium hydroxide (KOH) with impregnation ratio of 1:1 (KOH:char) in distilled water. Then, it was dehydrated in an oven at 105°C overnight. Dehydrated product was then incinerated in a tube furnace under the flow of nitrogen gas at 850°C for 2 hours. Once the temperature reached 850°C, the nitrogen gas was replaced by carbon dioxide gas, and this process was continued for 2 hours. The alkali activation shells powders (TS2) were kept in zipper bag before further experiments.

2.4 Preparation of Adsorbate

In this research, MG was chosen as an adsorbate. A stock solution of MG with a concentration of 1000 mg/L was prepared by dissolving 1g of MG powder in 1L of distilled water [8]. The working solutions of desired concentrations were then prepared by dilution using a volumetric flask [9].

About 500 mL of MG working solution with concentration of 50 mg/L was prepared from the stock solution. Whereas for optimization process for initial concentration of adsorbate, about 100 mL of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L MG working solutions were prepared separately.

2.5 Batch Adsorption Experiment

2.5.1 Effect of Contact Time

Eight different conical flasks containing 100 mL of 50 mg/L MG solution each with pH 7 were prepared. About 1 g of TS1 was added into each conical flask. After that, they were kept in the incubator shaker at constant speed of 150 rpm at 30°C, for time interval of 30 minutes, 60 minutes, 90 minutes, 120 minutes, 150 minutes, 180 minutes, 210 minutes and 240 minutes. After shaking, the solutions were filtered using filter paper.

The adsorbance of the remaining MG solutions was measured using UV-Vis spectrophotometer. The same steps were repeated by replacing TS1 with TS2.

2.5.2 Effect of initial pH of the solution

Five different conical flasks with 100 mL of 50 mg/L MG solution each were prepared. About 1 g of TS1 was added into each conical flask. The pH of the solutions was adjusted using 0.1 M HCl and 0.1 M NaOH solution with a pH meter. The pH values of the solutions were varying as 2, 4, 6, 8 and 10. The conical flasks were then being placed in incubator shaker with a speed of 150 rpm at 30°C. The contact time of adsorbent with MG solution was taken from the optimized contact time in the previous experiment. After the shaking, the solutions were filtered using filter paper.

The absorbance of remaining MG solutions was measured using UV-Vis spectrophotometer. The same steps were repeated by replacing TS1 with TS2.

2.5.3 Effect of Initial Concentration of Adsorbate

About 100 mL of MG solution with concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L were prepared separately and taken into five different conical flasks. About 1 g of AC 1 was added into each conical flask. The pH of MG solution was adjusted to optimized pH as previous experiment. They were then being placed in incubator shaker with speed of 150 rpm at constant temperature of 30°C, with an optimized contact time. After shaking, the solutions were filtered by using filter paper.

The remaining MG solutions' absorbance was measured by using UV-Vis spectrophotometer. The same steps were repeated by replacing TS1 with TS2.

2.5.4 Effect of Adsorbent Dosage

Five different conical flasks with 100 mL of optimized concentration of MG solution were prepared. Different dosage of TS1 ranging from 0.6 g, 0.8 g, 1.0 g, 1.2 g and 1.4 g was added to each conical flask. The initial pH of the solutions was adjusted to the optimized pH as previous experiment by using 0.1 M HCl and 0.1 M NaOH. The conical flasks were placed inside incubator shaker with speed of 150 rpm and the temperature was maintained at 30°C. The contact time for adsorbent and adsorbate was fixed according to the optimized contact time obtained in previous experiment. After shaking process, the solutions were filtered by using filter paper.

The absorbance of remaining MG solutions was then being measured by using UV-Vis spectrophotometer. The same steps were repeated by replacing TS1 with TS2.

2.6 Removal Efficiency

The removal efficiency of TS1 and TS2 was compared by calculated their MG dye removal percentage. The percentage of MG removal was calculated using the formula below;

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \% \quad (1)$$

where

C_0 = Initial MG dye concentration (mg/L) , C_e = Final MG dye concentration (mg/L)

3. Results and Discussion

3.1 Batch Adsorption Experiments

The batch adsorption experiments results on the effect of contact time, pH, initial concentration and adsorbent dosage were shown in Figure 1, Figure 2, Figure 3 and Figure 4.

Figure 1 showed the effect of contact time for MG removal. In the first 30 minutes, MG was rapidly adsorbed by both TS1 and TS2. As time increased the adsorption rate slow down, until the equilibrium state reached. In the beginning, the surface area of both types of activation has not yet occupied. MG molecules were adsorbed very fast at the exterior surface of both TS1 and TS2. This caused the adsorption rate was very fast initially. After 30 minutes, the exterior surface of TS1 and

TS2 was almost saturated and fully occupied by MG molecules. The dye molecules entered into the pores, and adsorb by the interior surface of TS1 and TS2. This process took relatively long period of time until both the equilibrium state was attained [10].

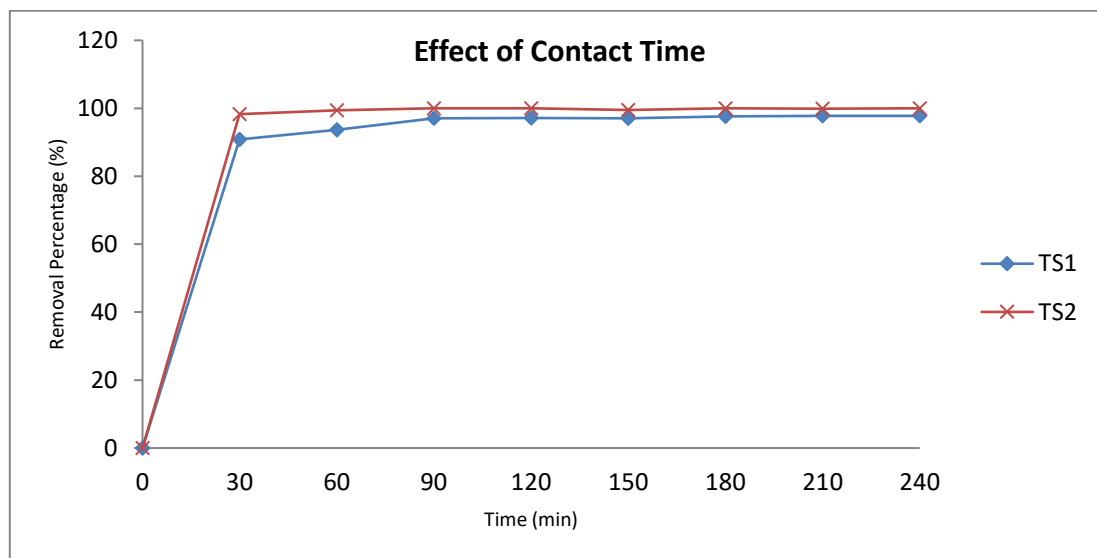


Figure 1. Effect of Contact Time

Optimum contact time for MG dye removal recorded by TS1 is 210 minutes, while for TS2, the optimum time recorded was shorter, which was 90 minutes. The percentage removal by TS1 and TS2 are 97.76% and 100% respectively, after their optimum contact time with MG solution. This may due to the different functional groups that existed on both types of activated shell powders, which contributed to better adsorption efficiency of TS2 with the shorter time needed to attain an equilibrium state.

Figure 2 shown the removal percentage of MG by TS1 and TS2, with varying initial pH ranging from 2 to 10. The previously optimized parameter (contact time) was brought forward, which was 210 minutes for TS1 and 90 minutes for TS2 (adsorbent dosage = 1.0 g; initial concentration = 50 mg/L). The results showed that at pH2, the removal percentage of MG was relatively low, which was 49.53% for TS1 and 86.79% for TS2. This probably due to the presence of large quantity of hydrogen ions, H^+ in acidic medium. Since MG is a cationic dye, it is positively charge in aqueous medium. A large amount of H^+ ions competing with the cationic dyes for adsorption sites on the activated shells powders, causing a declination in the amount of MG adsorbed on them [11]. Besides that, in low pH medium, the surface area of the activated shells powder was positively charged. The electrostatic repulsion between the same charge of the activated shells powder and cationic dyes was very high, which led to low adsorption rate of dye on them [12]. On the contrary, at high pH medium such as pH 10, the surface of both TS1 and TS2 became negatively charged, which lowered the surface charge density. This lowered the electrostatic repulsive force, and increased the electrostatic force of attraction between positively charged MG ions and negatively charge activated shell powders at the same time, results in the increase of adsorption rate and removal percentage of dyes [13].

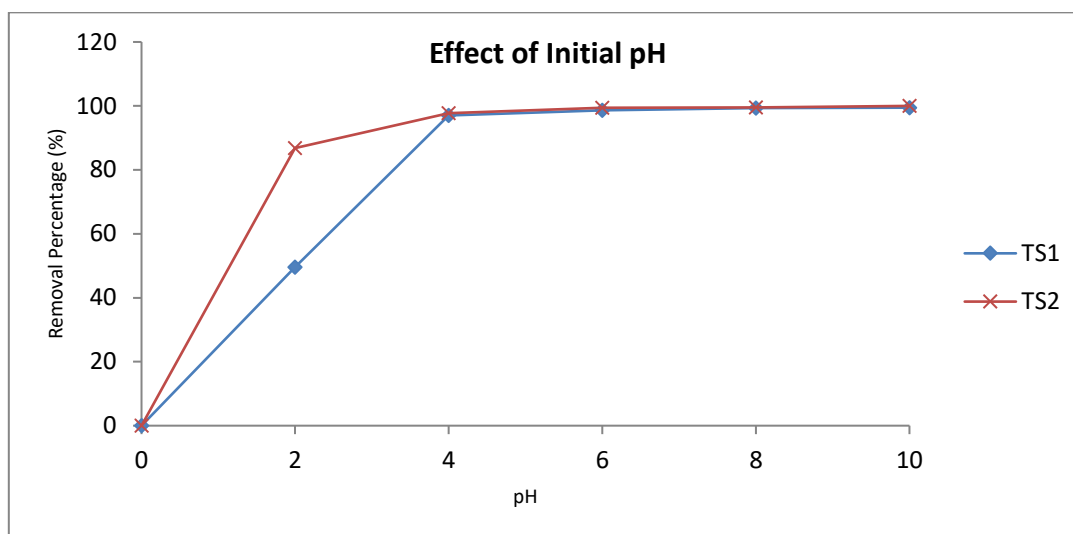


Figure 2. Effect of adsorbate initial pH

As the pH of MG aqueous medium increased, the removal percentage for TS1 and TS2 also increased. The optimum pH for TS1 in dye removal was pH 10, with removal percentage of 99.46%; while for TS2, the optimum pH was the same as TS1, with slightly higher removal percentage, which was 100%. Previous studies had proved that when the pH values increase, the adsorption of MG to activated carbon will also increase [5, 14, 15].

Since there is a limit for a given amount of adsorbent to adsorb dye, the initial dye concentration becomes one of the most important parameters to be investigated [16]. In this study, the experiment on the effect of the initial concentration of adsorbate MG on the removal efficiency by TS1 and TS2 was carried out. The previously optimized contact time was brought forward, which was 210 minutes for AC 1 and 90 minutes for AC 2. The optimum pH for both TS1 and TS2 was pH 10, while the adsorbent dosage for both types of adsorbents was still fixed at 1.0 g.

Figure 3 shown the removal percentage of MG by TS1 and TS2, for initial concentration varying from 10 mg/L to 50 mg/L. The graph shown the removal percentage of MG found to decrease as the initial concentration of adsorbate increased.

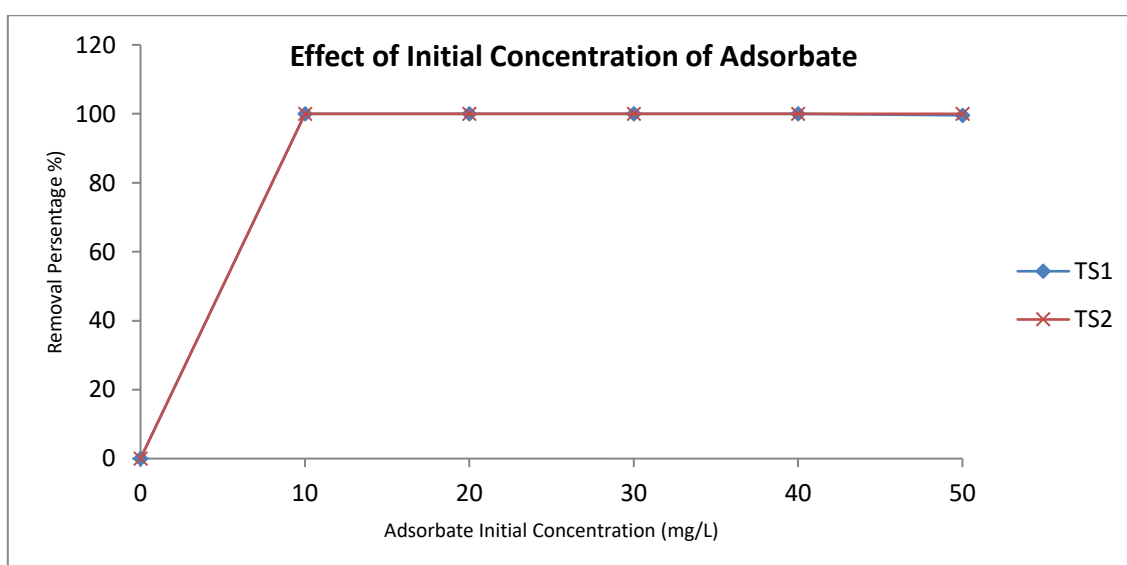


Figure 3. Effect of adsorbate initial concentration

For TS1, the removal percentage for MG with an initial concentration of 10 mg/L to 40 mg/L was 100%, and there was a slightly drop in removal percentage when the initial concentration increased to 50 mg/L, which was 99.59%. On the other hand, for TS2, the removal percentage of MG maintained at 100% for the initial dye concentration of 10 mg/L to 50 mg/L. This result showed that TS2 has greater availability of surface area compared to TS1. It had sufficient active sites for MG to bind on although the concentration of adsorbate was high.

In the last part of this study, the experiment of the effect of adsorbent dosage on MG dye removal was carried out. All the previously optimized parameters were combined to put into this last parameter. The conditions used were 210 minutes and 90 minutes of contact time for TS1 and TS2 respectively, and 10 mg/L of initial adsorbate concentration at pH 10 for both of them. Figure 4 shown the removal percentage of MG by TS1 and TS2, with a varied adsorbent dosage in the range of 0.6 g to 1.4 g.

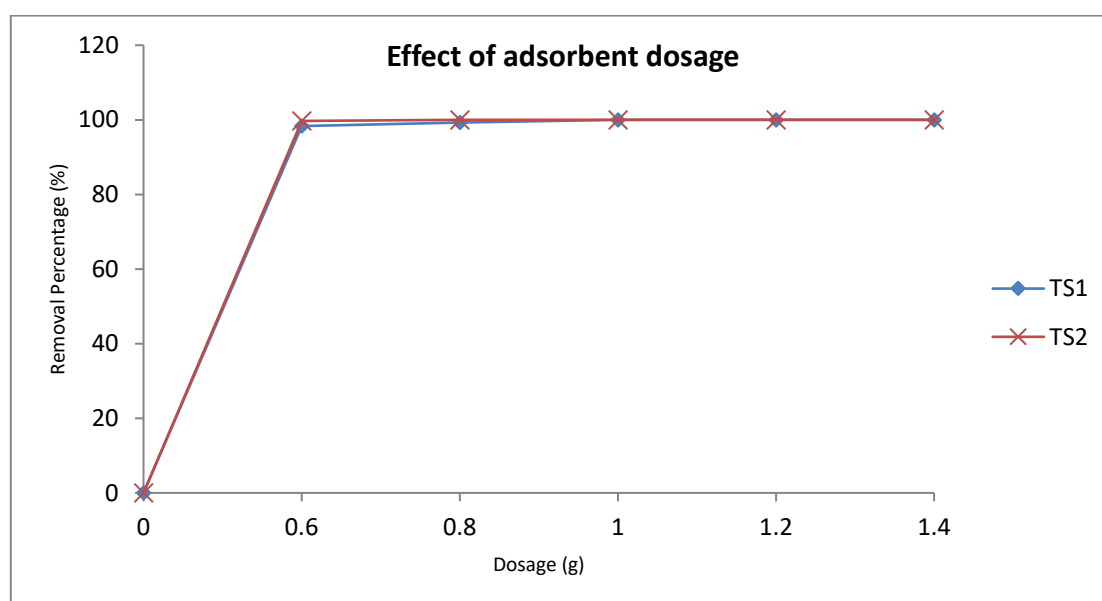


Figure 4.

As the amount of adsorbent increased, the removal percentage of MG was also increased, until they attained an equilibrium state, which was 100% of removal percentage in this study. TS1 required higher dosage (1.0 g) to remove all MG ions from aqueous solution. While TS2 required less dosage, which was 0.8 g to achieve 100% removal percentage. As there was an increment in adsorbent dosage, more surface area and active sites will be available [19]. This increased the binding sites that enable MG ions to bind on it [20]. Since the binding sites were in excess and the initial concentration of adsorbate was fixed, they remained unsaturated during adsorption reaction. Thus, more dye molecules can be adsorbed by the activated shell powders and higher removal percentage of MG can be achieved.

4. Conclusion

In conclusion, through the comparison between TS1 and TS2, the removal efficiency of TS2 is better than TS1. This may due to the different functional group presented at the surface of both activated shell powders. TS2 need less contact time and less dosage to achieve 100% removal percentage. While TS1 need longer contact time and slightly higher dosage to achieve 100% removal percentage. Both of them have high adsorption capability to remove MG from aqueous solution, but TS2 had better performance than TS1.

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