Adsorption of Methylene Blue on to Blue Water Lily Stalks

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Abstract - Present study reports a development of a novel cost-effective biomass material derived from blue water lily stalks (BWLS), *Nymphaea nouchali*, for the removal of non-biodegradable organic toxic pollutants, such as methylene blue (MB) from industrial effluents. The potential of the BWLS for the removal of MB from an aqueous solution was investigated in greater detail. Experiments were performed under various conditions including contact time, adsorbent dose, pH of the system, initial MB concentration, and temperature. Results were tested with the Langmuir, Freundlich, and Temkin adsorption isotherms to determine the most suitable adsorption model. Experimental data showed a perfect correlation with Freundlich isotherm with an R^2=0.996 representing possible multilayer adsorption. The maximum adsorption capacity of BWLS was found to be 200 mg/g at 303.15 K for an initial dye concentration of 1750 mg L^{-1}. The kinetic studies demonstrated that the adsorption obeyed a pseudo second-order model. The FT-IR spectra showed that a large number of hydroxyl groups (-OH) and carbonyl (C=O) were present on the surface. Point of zero charge for BWLS was greater than zero indicating larger negative charge distribution on the surface. The results were compared with activated charcoal (AC) at similar conditions and found out that BWLS were better. The present study demonstrated that BWLS was a promising material as a low-cost biosorbent for the removal of MB from an aqueous solution.

***Keywords: Adsorption, Blue water lily stalks, Methylene blue, Activated carbon, Isotherms, Kinetics*.**

I. INTRODUCTION

Water pollution is one of the major problems faced nowadays due to rapid industrialization. Untreated textile effluents, which are rich in dyes and chemicals, are dumped into waterways around the world. Most of such effluents consist of non-biodegradable and carcinogenic molecules which could pose a significant threat to human and aquatic health [1]. Further, an excessive amount of such dye molecules is able to destroy the aquatic ecosystem which causes the reduction of light penetration and hinders the photosynthetic activities of the first trophic level. Thus, removal of the synthetic toxic dyes from water is essential. Many studies are conducted for the removal of dyes such as membrane filtration, photodegradation ion exchange, and biosorption. However, the techniques have limitations and hence adsorption techniques are of interest which are easy, effective, and cheap [2]. This study focuses on adsorption of MB using blue water lily stalks (BWLS) as a promising adsorbent collected from waste sites.

II. MATERIALS AND METHODS

A. *Preparation of adsorbents*

The BWLS was collected from waste sites around the Bellanwila temple area in Sri Lanka. The collected biomaterial was carefully washed with tap water to remove any dust and other impurities followed by distilled water. The stalks were cut approximately 3 inches and then oven dried at 65 ºC (338 K) for 24 hrs. The dried stalks were ground, sieved into 100 nm particle-sized, and washed again to remove pigments present in the biomass. This washing was done for 3 days at a rate of 100 rpm in beakers. Finally, the washed materials were again oven dried at 65 ºC (338 K) for 24 hrs. And packed in cleaned containers. The containers were stored at room temperature for adsorption experiments.

B. *Preparation of dye solution*

The MB chloride [$C_{16}H_{18}N_3SCl$] was obtained from Loba Chemie India Pvt Ltd which had 98% assy. A 2.041 g of dye was dissolved in distilled water in 1 L volumetric to create a stock solution of MB with a concentration of 2000 mg L^{-1}. By applying serial dilutions, at a range of 750-1750 mg L^{-1} with 250 mg L^{-1} deviations.

C. *Adsorption experiments*

The adsorption studies were carried out in a batch process. The effect of initial dye concentration, temperature, contact time, and BWSL dosage was studied. The adsorption studies were carried out by adding a pre-weight 200 mg of BWSL to 25 mL of dye with a 1750 mg L^{-1} in a centrifuge tube. The mixture was agitated in a water bath shaker at 150 rpm for 2hr at a constant temperature. The supernatant solutions were analyzed using UV-Vis spectrometer at λ_{max} = 663 nm. The adsorption isotherm was plotted using dye solution (750- 2000 mg L^{-1}) at 303.15 K Kinetic experiments were also carried out at varying times until the equilibrium was reached. Characterization of biomaterial was done using FTIR.

III. RESULTS AND DISCUSSION

A. *Influence of initial dye concentration*

Variation of initial concentration showed that q_e for BWLS was increasing but for AC it reached a maximum and then decreased. As such the appropriate concentration was chosen to be 1750 mg L^{-1}.

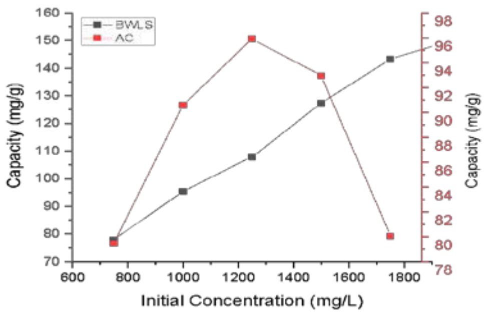

Fig. 3 Effect of initial concentration on adsorption of MB

B. *Influence of contact time*

The adsorption of MB was rapidly increasing in the first 30 min resulting in 54.68% of dye removal which reached equilibrium at a slower rate reaching a maximum of 66.2% removal with adsorption capacity (q_e) of 141.7 mg/g.

C. *Influence of temperature*

When the temperature was increased from 303.15 to 403.15 K, BWLS showed a linear increment in q_e and when the temperature was increased further a decrease in q_e was visible. The AC shows a linear variation with a positive slope. Overall results show that BWLS undergoes changes in the binding sites when the temperature was increased.

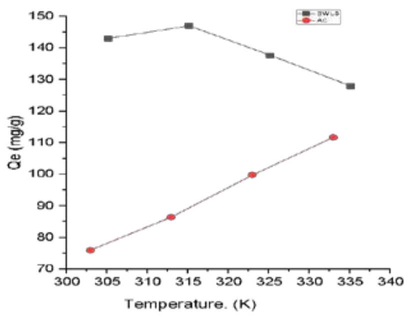

Fig 1- Variation of adsorption capacity with temperature.

D. *Equilibrium modeling*

The best-fit isotherm for BWLS was found the to be Freundlich model having a R^2=0.996 indicating probable multilayer formation. The maximum coverage adsorption capacity (Q_o) calculated shows that BWLS has 200 mg/g while AC has 86 mg/g at 303.15 K thus suggesting that BWLS is a better adsorbent material than AC.

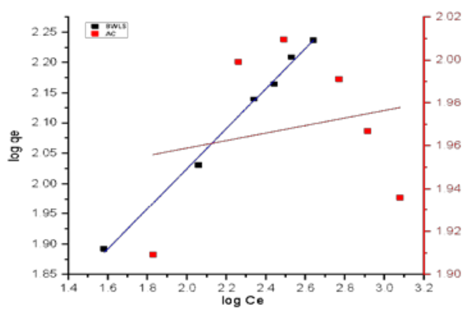

Fig. 2 Log Qe vs Log Ce, Freundlich plot at 303.15 K.

E. *Kinetic Study*

Pseudo first-order, pseudo second- order and intra particle diffusion models were evaluated in the present study. After the interpretation of the results, the pseudo second-order kinetic has the best correlation with R^2= 0.9998. This indicates the rate-determining step chemisorption. When the intra-particle diffusion plot was drawn, it showed that diffusion of adsorbate onto the micro pores takes place slowly, and thus the overall mechanism is a complex process.

D. *Influence of pH*

Increasing the pH from 4-10 showed a decrease in adsorption capacity from 157.9 - 131.5 mg/g. At higher pH, the surface of BWLS becomes negatively charged and the positively charged NH_3^+ fragments in MB get deprotonated. Then lone pair causes electrostatic repulsion and lowers the adsorption capacity.

E. *Effect of dosage*

As the BWLS powder concentration was increased from 8 to 20 g L^{-1}, the percentage adsorbed increased from 39.27% to 94 .10%. However, the q_e showed the opposite trend. The rate of removal increased due to the presence of increased surface area and the availability of more adsorption sites.

F. *Characteristics of Blue water lily stalks*

The FT-IR analysis shows the presence of a broad peak at 3348 cm^{-1} which is due to hydroxyl groups (-OH) in BWLS. The Comparison of spectra before and after adsorption illustrates unabsorbed the broad peak had turned into a sharper peak demonstrating the formation of more H- bonds with MB. Further, the presence of phenol groups can be confirmed due to the sharp peak at 1041.48 cm^{-1} which is due to –OH bending. The presence of a peak at 1643 cm^{-1} is due to carbonyl stretching[3]. The analysis shows that these functional groups can be potential active sites for the adsorption of MB.

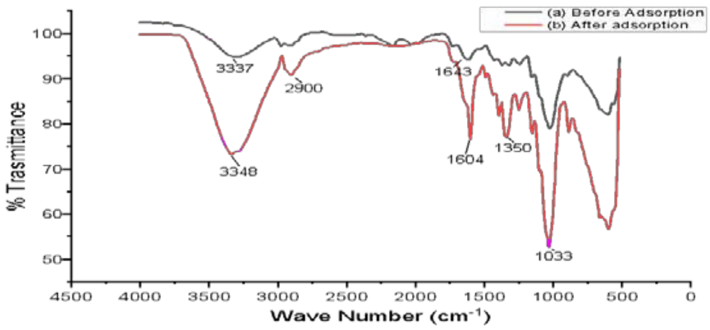

Fig 1- FTIR spectrum of BWLS (a) and BWLS absorbed MB (b)

IV. CONCLUSION

The present analysis reports a study for the adsorption of MB dye from wastewater using BWLS developed from waste materials as potential adsorbent which can be used as an alternative to activated carbon and other costlier adsorbents. Following the best correlation to Freundlich isotherms and having a maximum adsorption capacity of 200 mg/g at 303.15

K. The adsorption kinetic study follows pseudo-second order having chemisorption as the rate determining step.

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