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Adsorption of Malachite Green using Nitric Acid Activated Bio Adsorbent from Corn Cob Husk

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***Abstract*— In this paper, exploitation of the Malachite Green (MG) dye to aquatic solutions through nitric acid-activated corn cob husk (CCH) will minimise outlays for biosorbent recovered by the valorization of agro-residues. The key parameters were optimized through batch experiments and gave the highest removal efficiency of 98.13% at pH 5.89, 90 minutes contact time, 20mg/L preliminary concentration and 0.25g/100 mL adsorbent amount, and the adsorption capacity was 16.62mg/g in higher concentrations. The model of adsorption that best fits the equilibrium data was the Langmuir adsorption isotherm (R2 = 0.98), which point to surface assimilation of the same kind proceeding on the monolayer alongside maximum adsorptive power of 101.01mg/g and a desirable separation factor (0 < RL = 1). The process exhibited great ability to treat textile wastewater by exploiting waste valorization to achieve efficient and environmentally friendly dye decolourization.**

***Index Terms*— Malachite Green (MG), Corn Cob Husk (CCH), Activated Carbon, Dye Adsorption, and Textile Effluent Removal.**

I. INTRODUCTION

A. Environmental Pollution from Industrial Dyes

The outcome of the rapid population increases and industrial growth is the escalation of environmental pollution, during which the industries of textile, cosmetic, paper, leather, tannery, and plastic release dyes into the air, water, and soil [1]. Wastes in textile factories carry dyes, chemicals used in the treatment process, dyeing, printing, and finishing, rising need for chemical and biochemical oxygen and stopping sunlight from entering water [2]. Adsorption is a potent, low-cost, eco-friendly dye removal method, which uses corncobs, abundant in cellulose, hemicellulose, and lignin, converted into activated carbon through carbonization [3][4].

B. Toxicity of Malachite Green and Research Focus

Figure 1. The structural formula of MG dye

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One such toxic cationic triphenylmethane (C23H26N2Cl) dye is malachite green (MG) is shows in Fig. 1, which endures in textile and aquaculture effluents, damaging organs, causing cancers, and causing endocrine disorders in mammals [5]. Its inability to biodegrade and be detected in the wastewater requires the adsorption with low-cost maize cob adsorbents [6]. In this paper, corn-cob husk is assessed to decolourize MG based on textile effluents, and the adsorption parameters and equilibrium behaviour are optimized [4].

II. METHODOLOGY

A. Preparation of Activated Corn Cob Husk with Nitric acid

Corn cob husks from nearby sources were sequentially cleaned to create nitric acid-activated corn cob husk (CCH), thermal treatment, acid activation, and size reduction in a controlled workflow suitable for adsorption studies. Briefly, husks were thoroughly rinsed with deionised water, sun-dried, and desiccated at 105–110°C for 24 hours to remove wetness, then chilled in a moisture-controlled atmosphere after being carbonized for 30minutes at 300°C in a muffle furnance. The carbonised cinder did chemically react with HNO3, rinsed alongside demineralised water to a balanced pH, desiccated again at 105–110°C, and finally ground to a 210–300μm powder for use as an adsorbent. Similar pretreatment, carbonization, acid washing/neutralization, and drying steps are standard in the literature for corn-derived activated carbons used in water treatment applications [7].

B. Adsorbate Preparation

The preparation of adsorbates was done through initially preparing a malachite green (MG) stock solution by dissolving a notable weight of dye in purified water to form a precise immersion. Working solutions (10, 20, 30, 40 and 50 ppm) were prepared using this stock through serial dilution and these standard solutions were then used to develop a calibration curve to be used in future experiments of adsorption[8].

C. Adsorption Studies

Equilibrium Studies

Standard adsorption protocols were used to conduct batch equilibrium tests at 30°C and 150 rpm agitation to optimize major scopes such as pH, connection time, preliminary MG concentration and adsorbent amount. Parameters were manipulated one by one, and the rest held constant in order to determine the best conditions, and residual dye concentration did calculated using UV-Visible spectrophotometry at a wavenumber λ_max= 621nm following filtration. The equilibrium data were analysed using relevant adsorption isotherm models (Table 1)[9].

D. Isotherm Studies

Adsorption isotherms Characterize the dispersion of ascorbate between the firm adsorbent surface and the fluid phase at a fixed temperature, which characterises the most adsorptive power and the interaction process. Models, including Langmuir and Freundlich, explain the surface coverage, heterogeneity, and binding affinity that are valuable in order to maximize processes of dye removal in wastewater treatment [10].

$$\%\, Removal = \frac{C_o - C_e}{C_o} x100 \quad \text{..... Eq. 1}$$

$$q_{max} = \frac{(C_o - C_e)V}{W} \quad \text{..... Eq. 2}$$

TABLE I. ADSORPTION ISOTHERM INVESTIGATION

Models	Nonlinear form	Linear form
Langmuir Isotherm	$j_e = \frac{a_m + M_L + B_e}{1 + M_L + B_e}$	$\frac{B_e}{j_e} = \frac{1}{M_L a_m} + \frac{B_e}{a_m}$
Freundlich Isotherm	$j_e = K_f {B_e}^{1/n}$	$\log j_e = \log K_f + \frac{1}{n} \log q\, B_e$

III. RESULT AND DISCUSSION

A. FT-IR Evaluation

The FT-IR evaluation was done for resolve the operable groups that were included in the adsorption process. Fig. 2 of the FT-IR spectrum shows that different operable groups exist above the adsorptive surface, as evidenced by the presence of the peak before and after adsorbing malachite green. The alteration of the spectra can be viewed

as an indication of the malachite green being attached to the corn cob husk (CCH), which means that the adsorbate and adsorptive operable groups interact well and that the adsorption process is indeed improved. The variations are important in the ion exchange and dye binding during biosorption at advanced adsorption stages. The broad range of O-H stretching bands at (3733-3663) cm-1 indicates the existence of alcohol and phenolic groups. This extension is a result of the adsorption of malachite green to the corn cob husk (CCH). The bands projected in the range of (918 -1003) cm-1 may be identified as the stretch of bonds C = O. The proliferation of the number of oxygen-containing operable groups on corn cob husk (CCH), which might be due to the oxidation process by acids, could further increase the dye binding capacity by using the biosorption process.

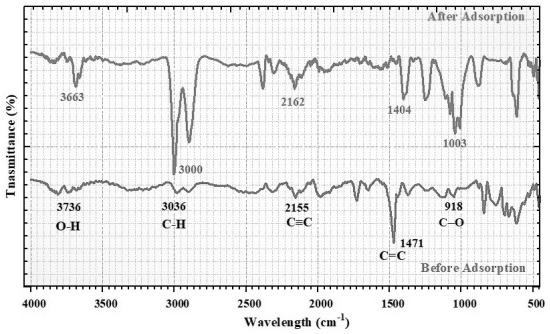
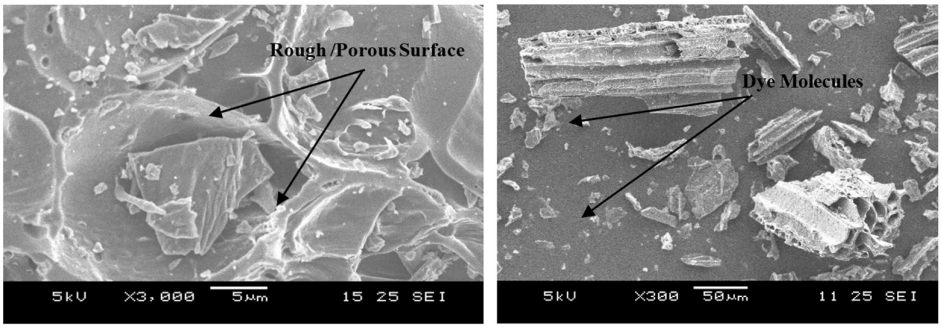


Figure 2. FT-IR Spectrum CCH pre and post adsorption.

B. Field Emission SEM Evaluation

The Field Emission-SEM images of the micromorphological features of corn cob husk (CCH) in malachite green adsorption are shown in Fig. 3 (a) and (b) as the images depict the before-malachite green adsorption and after-malachite green adsorption, respectively. The irregular and rough surface that was witnessed in the case of CCH adsorbent could be explained by the activation of nitric acid, which is likely to increase the adsorption efficiency of dye particles above the adsorbent surface. Activated adsorbents, which are acid-catalysed, tend to have greater adsorption capacity and better contaminant removal because they have better surface properties, increased ion-exchange behaviour, and have more active irrevocable sites. The surface morphological feature that indicates the presence of comparatively smooth surface following deposition is a manifestation of the adsorbed dye molecules on the adsorbent surface.



Before-Adsorption After-Adsorption

Figure 3. Field Emission-SEM Evaluation (a) Before-Adsorption and (b) After-Adsorption.

C. Impact on Contact Time

Contact time was studied with Malachite Green on CCH adsorbent at 30 0.5 o C, 150 rpm, pH 5.89, agitation rate 150 rpm, dosage rate of adsorbent 0.25 g/100 mL, and preliminary immersion of dye 10mg/L under 30-150 minutes. As shown in Fig. 4,the results showed that the adsorption capacity increased to 3.89mg/g and 3.86mg/g, and the removal effectiveness increased to 97.47 percent with contact time increasing in the same manner (30 to 90 minutes). The fact that there were more vacant active sites on the adsorbent's surface provided clarification. After 90 minutes, the removal was slightly lower and was 96.31%, possibly because of fewer available sites and more resistance to mass transfer. Thus, the duration of contact of 90 minutes was chosen as the best to use in additional experiments.

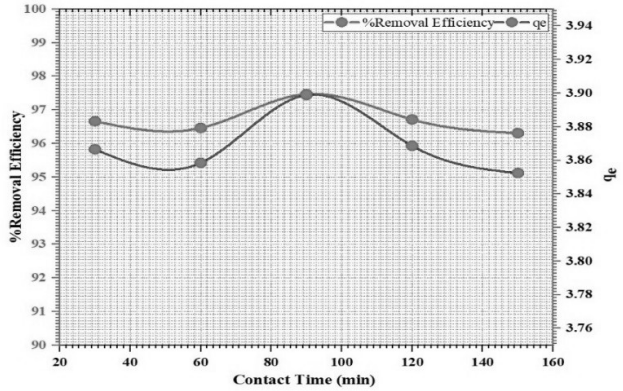


Figure 4. Evaluation of contact time

D. Impact on Preliminary Concentration of Dye

Initial concentration of dye was analysed on the Malachite Green adsorption on CCH adsorbent at an optimal contact time of 90 minutes, pH 5.89, temperature of (30±0.5)°c, agitation rate of 150rpm, and adsorbent dose of 0.25g/100mL as conditions were varied between the lowest dye immersion of 10mg/L and the highest dye concentration of 50mg/L. Fig. 5 disclosed that the adsorption power rose alongside an increase in concentration, from 3.87mg/g to 16.62mg/g due to a higher driving force of mass transfer, and the adsorption power increases with concentration. The efficiency of removal increased by a factor of 96.86 to 97.81percent with the increase of the concentration between 10 and 20mg/L. Nonetheless, the maximum removal rate was clustered to 83.10 per cent at a higher immersion of 50mg/L of the adsorbent because of active site saturation on the adsorbent surface. This tendency could be explained by the fact that as dye molecule concentration rises, fewer adsorption sites are available.

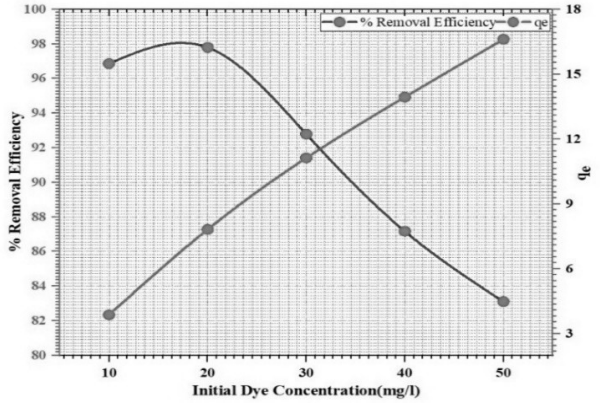


Figure 5. Investigation of initial dye concentration.

E. Impact on Adsorbent Dose

The dosage of adsorbent was studied on Malachite Green elimination through CCH adsorbent under the ideal conditions of an interaction time of 90 minutes, pH 5.89, 20 mg/L dye concentration, and temperature (30±0.5) °c and an agitation speed of 150rpm. The removal efficiency of different dosages was found to increase with the dosage, with a maximum of 98.13% at 0.25 g dosage compared to 0.15 g dosage, as seen in Fig. 6, and this can be examined by the dosage's increase in the number of active sites and surface area accessible for adsorption. At 0.45 g, a slight reduction was noticed to 96.56%, which was probably because of surplus adsorbent that resulted in overlapping of the particles and lesser active adsorption. As the dosage increased, the adsorption capacity dosage dropped, changing from 12.72mg/g to 4.29mg/g. The cause of this decrease is the saturation of the site with the increased dosage, redistribution of vacant dye molecules across a greater mass of adsorbent and potential aggregation of the particles, which reduces the net available surface area. Such findings show that 0.25 g/100 mL offers the best balance between the elimination productivity and the adsorption power.

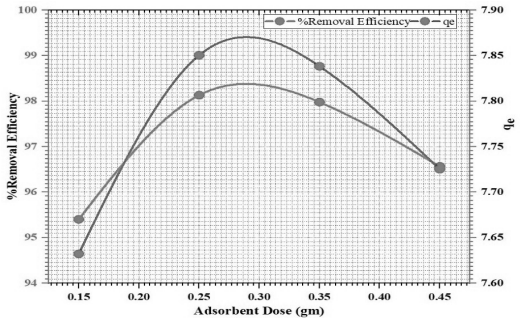
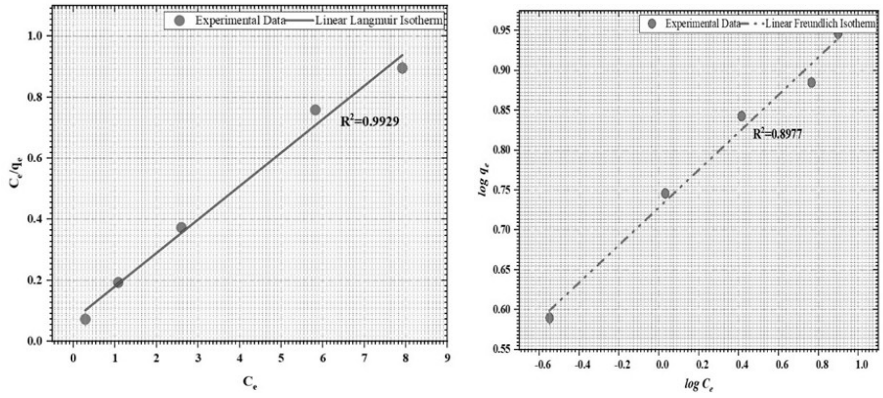


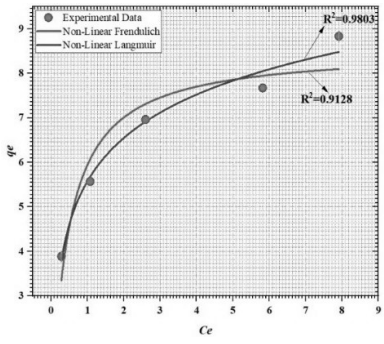
Figure 6. Investigation of Adsorbent dose

F. Adsorption Isotherm Analysis

The equation of adsorption equilibrium in the Malachite Green removal by nitric acid modified corn cob husk was assessed according to both linear and non-linear forms of both the Langmuir and the Freundlich model, as illustrated in Fig. 7. Both fitting methods gave a capability of 101.01mg/g of monolayer adsorption of the system, which was described by the Langmuir model. The separation factor $(0 < RL < 1)$ ensured that absorption did, and beneficial and strong correlation coefficients (R2 = 0.9929 in the linear and 0.9803 in the non-linear) showed the appropriateness of the model. Analysis through the Freundlich revealed that the adsorption was on heterogeneous surfaces with a Kf value of 5.57 mg/g and adsorption intensity (n = 4.17), indicating favourable uptake. But the correlation coefficients (R2 = 0.8977 linear and0.9128 non-linear) were lower than those of Langmuir, indicating that, even though surface heterogeneity was a factor in the process, the dominant factor is monolayer adsorption. These data show that the association between MG and CCH is regulated by both strong affinity to the similar active sites and other minor inputs of heterogeneous interactions on the surface.



(a) The Linear Isotherm (b) The Freundlich Isotherm



(c) The Nonlinear Isotherm

Figure 7. Adsorption Isotherm Linear (a) The Langmuir-Isotherm (b) The Freundlich-Isotherm (c)The Nonlinear Isotherm

IV. CONCLUSION

This experiment proved that bio-adsorbent corn cob husk developed with the activation of nitric acid is a good and cheap substance that could be used to extract the dye malachite Green from water. At ideal pH 5.89 and 90 minutes of contact time, the adsorbent made with heat and chemical activation demonstrated good removal efficiency, 20mg/L dye concentration and 0.25 g/100 mL dosage. There was a growth in adsorption capacity with the initial high dye concentration, which supported the existence of acute driving forces in mass transfer, and optimum dosage offered the best available surface capacity, with the onset of aggregation in the particles.
The equilibrium results were very much consistent with the Langmuir isotherm, which implied unilayer adsorption above homogeneous face alongside maximum power of 101.01mg/g and favourable RL values. The Freundlich model supported that there were heterogeneous binding sites, but showed lesser correlation, and this affirmed that monolayer adsorption controlled the process. These findings indicate that there is a high affinity between MG molecules and the activated corn cob surface and show that agricultural waste products can be converted to value-added adsorbents efficiently. All in all, it can be stated that the treatment of dye-contaminated wastewater using nitric acid-treated corn cob husk presents a sustainable and environmentally friendly solution.

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