REMOVAL OF REACTIVE ORANGE 16 FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO ACTIVATED CARBONS PREPARED FROM WASTE COCONUT FLOWERS

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Abstract: **Coconut tree flowers waste was investigated as a low-cost and effective adsorbent for the adsorption of Reactive Orange 16 from aqueous solution. Physico - Chemical characteristics of the adsorbents were studied as per the standard testing methods. Effect of various parameters such as agitation time, adsorbent dose and concentration, pH, temperature have been investigated in the present study. The adsorption of dyes have been best described by pseudo second order kinetic model and Langmuir adsorption Isotherms. The negative values of the ΔG^o and positive value of the ΔH^o indicate that the sorption process is spontaneous and endothermic in nature. The positive value of ΔS^o shows the increasing randomness during adsorption process. Desorptive studies reveals that no satisfactory desorption taking place indicating chemisorptive nature of adsorption.**

Keywords: **Reactive Orange 16, Coconut flowers, Adsorption.**

1. INTRODUCTION

Pollution caused by textile wastewater is a significant environmental challenge faced by many countries. Dyes used in the textile industry are particularly difficult to remove through conventional wastewater treatment methods due to their high stability against light, oxidizing agents, and resistance to aerobic digestion. To address these challenges, several advanced wastewater treatment schemes have been proposed for water quality enhancement. These treatment methods commonly employ a combination of biological, chemical, and physical processes. Among these, the activated carbon adsorption treatment has been established as an effective approach, though it incurs relatively high costs. This has driven the search for low-cost alternatives to activated carbon, spurring numerous studies on innovative materials[1-4].

India is the third largest producer of coconut in the world. Coconut tree flowers constitute as much as 80% of the coconut tree. The coconut tree flowers are waste materials after pollination.Coconut tree (*Cocos nucifera*) as precursor for the preparation of activated carbon. It was carbonized using phosphoric acid and activated.

2. MATERIALS AND METHODS

2.1 Preparation of the Adsorbent

Waste flowers of coconut flowers were collected then sun dried and stored in airtight plastic container for phosphoric acid activation. The sun dried coconut flowers were milled. This powder was mixed with 15% phosphoric acid in the weight ratio 1: 3 and heated to maintain a temperature of 450°C. The carbonization and activation completed by heating for 12hours and the resulting carbon was washed with distilled until a constant pH of the slurry was reached. The carbon was then dried for 6 hours at 100°C. The dried material was ground and used as adsorbent.

2.2 Preparation of the adsorbate

Stock solutions of 1000 mg/L of the Reactive Orange 16 dye were prepared by dissolving the dye in doubly distilled water. Working solutions at appropriate concentrations were prepared by diluting the stock solution.The reagents and chemicals were used are of analytical grade (AR).

2.3 Characterization studies

The functional groups present in the activated samples were detected by Fourier-transform infrared spectrometer (PerkinElmer spectrum two) [5-9]. The micro structures of the adsorbent were observed by SEM (JOEL Model: JSM 6360) and are shown in Fig.1. This figure shows that the adsorbent had an irregular and highly porous surface, indicating relatively high surface areas.
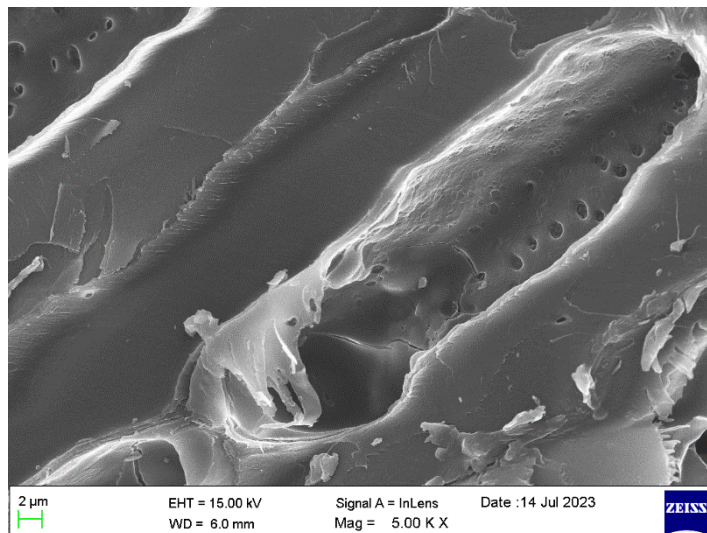

Fig. 1: SEM Image of the Adsorbent

2.4. Adsorption studies

Adsorption experiments were conducted using the batch method at temperatures of 302 K, 307 K, 312 K, 317 K, and 322 K. A known weight of the adsorbent was introduced into 50 mL of dye solution with initial concentrations ranging from 10 to 40 mg/L. The contents were thoroughly shaken using a mechanical shaker operating at 120 rpm for 100 minutes. The unadsorbed supernatant liquid was analyzed for residual dye concentration using a UV-Visible Spectrometer (JASCO V750). The pH of the adsorptive solution was adjusted using 0.1 N NaOH and 0.1 N HCl, measured with a Deluxe pH Meter (Model 101E). All experiments were conducted in duplicate, and the mean values of the two measurements were used for calculations.

2.5. Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent[10]. Desorption studies as a function of pH were conducted to analyze the possibility of reuse the adsorbent for further adsorption and to make the process more economical. After adsorption experiments the dye loaded adsorbent was washed gently with double distilled water to remove any un-adsorbed dye if present. Desorption studies were conducted using several such samples.500mg of the dye loaded adsorbent agitated above the equilibration time with 50ml of double distilled water of various pH.

3. RESULTS AND DISCUSSION

Adsorption of Reactive Orange 16 using Coconut flowers

3.1 Effect of Initial Dye Concentration and Agitation Time

The effect of agitation time and initial concentration on sorption at pH is depicted in Fig. 5. The percent sorption exhibited a increasing trend as the agitation time increased and reached an equilibrium state at 90 minutes is found sufficient and also invariant for equilibrium for various initial concentrations of dye 10,20,30,40 mg/l. The sorption capacity of activated carbon of coconut flowers is found to be greater than those of other activated carbon obtained from other materials [11].
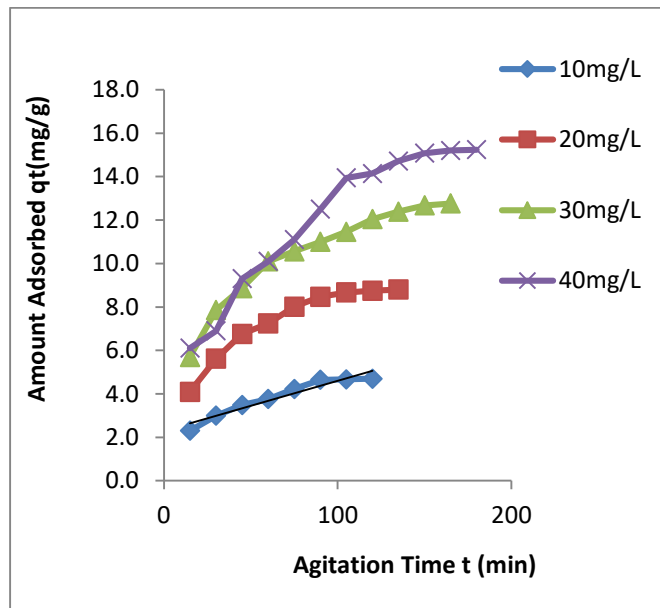
Fig. 2: Influence of Concentration

3.2 Effect of Sorbent dosage

The effect of sorbent dosage on dye uptake was investigated (Fig.3) and the rate of sorption increases with increase in dose of adsorbent. This is due to the increase in active sites for adsorption of dye molecules with increasing sorbent dosage[12]. The sorption equilibria of the dye were reached at 100 mg/l and the removal of dyes remained almost invariable above this dosage.Therefore100 mg/l appears to be the optimum sorbent dosage for the studied conditions.
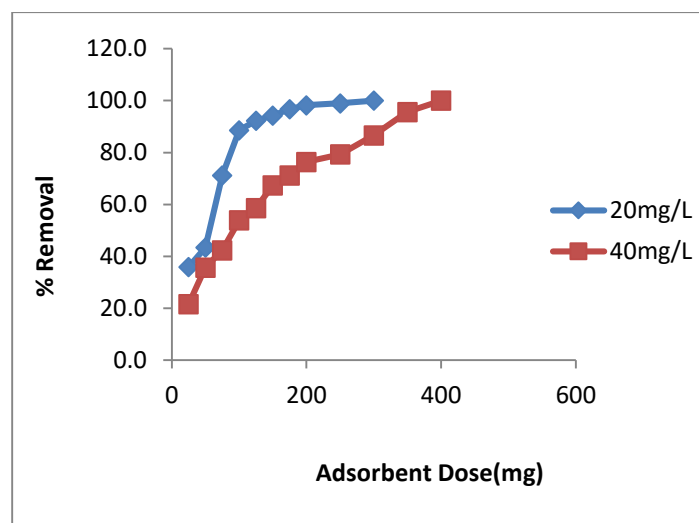

Fig.3: influence of adsorbent dosages

3.3 Effect of pH

The pH factor plays a critical role in the adsorption process, particularly for dye adsorption. The effect of pH on the adsorption of Reactive Orange 16 with coconut flowers was studied, revealing a significant influence on the adsorption process (Fig.4). The maximum uptake of Reactive Orange 16 was observed at pH 10, with a removal efficiency of 90%. Within the pH range of 3 to 7, the removal efficiency increased from 45% to 80%. However, as the pH increased from 7 to 10, the removal efficiency slightly decreased. The low adsorption of Reactive Orange 16 at acidic pH is attributed to the presence of excess H^+ ions in solution.
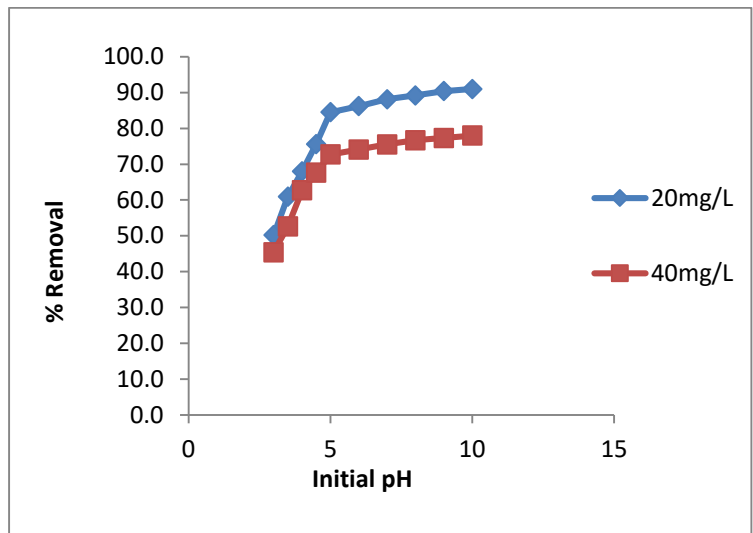
Fig. 4: Influence of initial pH of dye solution

At low pH levels, the percentage of dye removal decreases for cationic dye adsorption, whereas for anionic dyes, the removal efficiency increases. For cationic dyes, the reduced adsorption at acidic pH is likely due to excess H^+ ions competing with the cation groups on the dye for adsorption sites[13]. As the pH of the solution increases, the surface charge density of the adsorbent decreases, resulting in reduced electrostatic repulsion between the positively charged cationic dye and the adsorbent surface. Consequently, the removal efficiency improves.

3.4. Sorption Kinetics

The kinetics and dynamics of the adsorption of Reactive Orange 16 dye onto coconut flowers were studied using the pseudo-first-order and pseudo-second-order models (Fig.5) [14].

Pseudo-First-Order Equation

The sorption process was initially analyzed using the Lagergren pseudo-first-order rate expression:

$Log(q_e – q) – log\ q_e = k_1\ t\ /\ 2.303$ ……………………………………… ……… (1)

Where:

- q_e and q (both in mg/g) are the amounts of dye adsorbed at equilibrium and at time t, respectively.

- k_1 is the adsorption rate constant.

Plots of log $(q_e − q)$ versus time t were generated at varying temperatures and initial dye concentrations. However, experimental data did not align well with the pseudo-first-order model (Equation -1) across the full range of contact times, suggesting that this model does not adequately describe the kinetics of the adsorption process.

Pseudo-Second-Order Equation

The adsorption process was also analyzed using the pseudo-second-order kinetic model, expressed in its linearized form as:

$t/q_t = 1/k_2 q_e^2 + t/q_e$

Where:

- k_2 is the rate constant of second-order adsorption (g/mg/min).

- q_e is the amount of dye adsorbed at equilibrium (mg/g).

- t is the contact time (min).

Based on the results (Fig.5), the pseudo-second-order kinetic model provides a much better fit for the adsorption of Reactive Orange 16 by coconut flowers than the pseudo-first-order model.
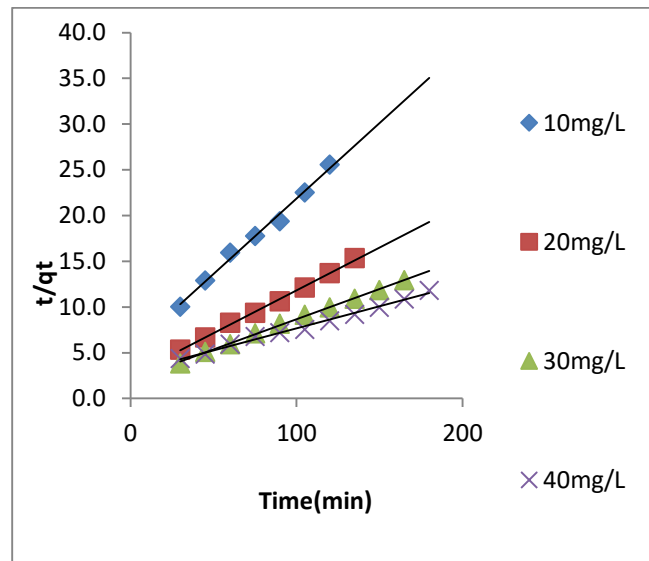
Fig. 5: Pseudo second order Kinetic Model

3.5. Sorption Isotherm

The adsorption data were analysed with the help of the following linearised forms of Freundlich and Langmuir isotherms .

Freundlich   isotherm : $\log q_e = \log K + 1/n \log c_e$

Langmuir isotherm: $c_e/q_e = 1/Q_o b + c_e/Q_o$

Where

 K=adsorption capacity

$(1/n)$=order/intensity of adsorption

 q_e =amount of dye adsorption per unit mass of adsorbent (mglg)

 c_e =equilibrium concentration of dye (ppm)

Q_o=monolayer (maximum) adsorption capacity (mglg)

b=Langmuir constant related to energy of adsorption (l/mg)

The values of Freundlich and Langmuir parameters have been obtained respectively, from the linear correlation between the values of (i) $\log q_e$ and $\log c_e$ and (ii) (c_e / q_e) and c_e (Fig.6 and 7).
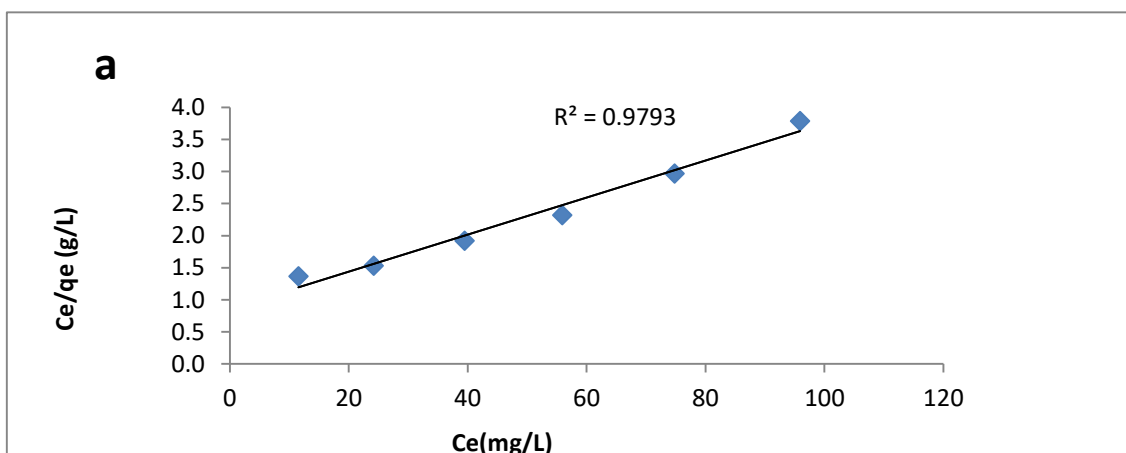
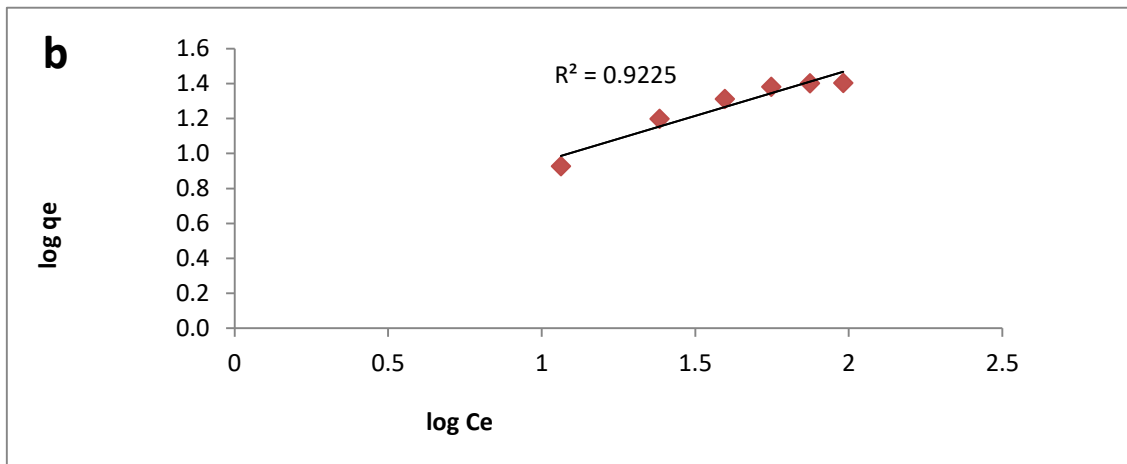

Fig. 6: Langmuir Isotherm

Fig. 7: Freundlich Isotherm

3.6. Effect of Temperature

Increase of temperature hardly increased qe value. The thermodynamic parameters was determined using the following equations.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta G^{\circ} = -RT \ln K_c$$

The negative value of Gibbs free energy change (ΔG°) indicates the spontaneous nature of adsorption[15].The results are shown in Fig.8.
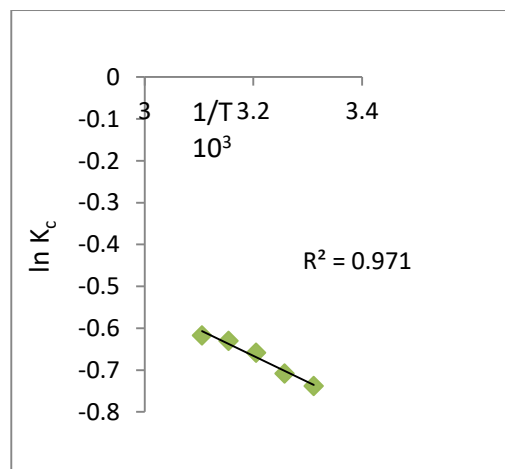

Fig. 8: Eyring's Plot

3.7. Intra Particle Diffusion Study

The possibility of intra particle diffusion process was explored by using the Weber and Morris intra particle diffusion model is,

$$q_t = k_i t^{0.5} + C$$

where

q_t - Amount of dye adsorbed at time t (mg/g)

C - intercept

k_i - intra particle diffusion rate constant(mg/g/min$^{-1/2}$)

The value of C gives an insight into the thickness of the boundary layer. Large intercept suggests great boundary layer effect. Similar results were reported in literature [16-17].

3.8. Desorption studies

To test the reversibility of the adsorbed dye molecules, desorption experiments were done using water, dil.HCl and dil.AcOH as the desorbing agents[17-19] . For this dye loaded adsorbent particles, after filtration, were kept in contact with 50ml of desorbing solutions for 4 hours and concentrations of dyes extracted were determined. Among these acetic acid was found to be better desorbing agent, it may be concluded that the dye must be attached to the adsorbent through an interaction of chemisorptions type.

4. CONCLUSION

This study underscores the potential of cotton stalks as a sustainable and efficient adsorbent for the removal of Reactive Orange 16 dye from industrial wastewater. The rod-shaped morphology and amorphous structure of coconut flowers contribute significantly to their adsorption capacity, with removal efficiency exceeding 90%. Key factors such as sorbent dosage, temperature, and initial dye concentration were shown to influence the sorption process, while the optimal pH range was determined to be between 3 and 7. The endothermic nature of the process further emphasizes its viability across varying operational conditions. Given their abundance, low cost, and non-toxic properties, coconut flowers offer a promising and eco-friendly solution for wastewater treatment. This approach not only provides an effective means of dye removal but also promotes the utilization of agricultural waste, aligning with principles of environmental sustainability and circular economy.

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