



Removal of Direct Red Dye Using Neem Leaf Litter

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Abstract:

The adsorption of Congo red (CR) onto carbon prepared from Neem leaf litter (NLLC) and Raw Neem Leaf Litter (RNLL) was investigated. The CR adsorption increased with an increase in pH of the CR solution in high acidic region and then decreased for NLLC, and for RNLL it slightly increased but rapidly decreased in neutral pH region but with further increase in pH, increased rapidly again. The Langmuir isotherm model showed a good fit with the equilibrium experimental data and the values of the heterogeneity factor (n) indicated heterogeneous adsorption of CR onto both RNLL and NLLC. The kinetic data showed better fit to the pseudo second-order rate model than to the pseudo first-order rate model in both cases. The adsorption of Neem leaf litter carbon (NLLC) showed the higher adsorption capacities of CR compared to Raw Neem Leaf Litter (RNLL) and any other adsorbents and would be a good method to increase adsorption efficiency for the removal of anionic dyes in a wastewater treatment process.

Background:

Wastewater effluents from different industries such as textiles, rubber, paper and plastics, contain several kinds of synthetic dyestuffs [1]. Further, discharging even a small amount of dye into water can affect aquatic life and food webs due to the carcinogenic and mutagenic effects of synthetic dyes [2]. Congo red [1-naphthalene sulfonic acid, 3, 30-(4, 40-biphenylenebis (azo)) bis (4-amino-) disodium salt] is a benzidine-based dye. This dye has been known to cause an allergic reaction and to be metabolized to benzidine, a human carcinogen.

Adsorption is quite popular due to simplicity and high efficiency, as well as the availability of a wide range of adsorbents. It has proved to be an effective method for removal of dye from wastewater [3].

Keyword: Adsorption, *Azadirachta indica* (Neem), Carbonization, Congo red.

Activated carbon is the most popular adsorbent for removal of dyestuffs from wastewater [4]. There is a growing need to find locally available, low cost, and effective materials like bentonite [5], rice hull ash [6], leaf [7], fly ash [8], activated red mud [9], rice husk [10], and fungi [11, 12] for the removal of dyes. Neem (*Azadirachta indica*) is an indigenous plant of Asian subcontinent known for its useful medicinal properties since ancient times. Neem leaf litter is an agro-industrial residue that left behind as waste. In this work, the potential of Carbon derived from Neem leaf litter and also Raw Neem Leaf Litter as an adsorbent on the removal of Congo red dye was investigated.

Materials and Methods:

Preparation of Neem leaf litter adsorbent:

Neem leaf litter was collected from KCT campus at 150°C overnight for carbonization and was used and washed it with acetic acid to increase the accessibility for adsorbate to adsorb. Then it was washed with distilled water several times to remove excess acid present. This part was split into two parts. One part was used as Raw Neem Leaf Litter powder. Another part was then kept in hot air oven as adsorbent for experiment.

Preparation of congo red (CR) solution:

A stock solution (1000 mg/l) of congo red (CR) was prepared in deionized water, and experimental solutions of desired CR concentrations were obtained by successive dilutions. The concentration of CR in the experimental solution was determined from the calibration curve prepared by measuring absorbance of different predetermined concentrations of CR solutions at λ_{max} of 570 nm using a DR5000 spectrophotometer (HACH, USA)

Batch Adsorption Studies:

Effect of Contact Time:

The effect of contact time was studied to determine the time taken by adsorbent to reach equilibrium at pH 5 with the initial CR concentration fixed at 400 mg/l. The CR concentration was measured at periodic time intervals (10 min) up to 50 min. Each data point

was obtained from an individual flask, and therefore no correction due to withdrawn sampling volume was necessary.

Effect of Initial Dye Concentration:

Equilibrium isotherm studies were carried out with different initial concentrations of CR (100 – 500 mg/l) at 30°C and pH 5. Langmuir and Freundlich isotherms were used to analyze the equilibrium adsorption data. The amount of CR adsorbed (mg/g) was calculated based on a mass balance equation as given below:

$$q = (C_o - C_f) \times V / m \tag{1}$$

Where,

q is adsorption capacity in mg/g,

C_o is initial dye concentration in mg/L,

C_f is final dye concentration in mg/L, V

is volume of final solution in mL, m is

the quantity of adsorbent in g.

Percentage Dye Removal = (C_o - C_f) x 100/C_o

Effect of pH:

The influence of pH on CR removal was studied by varying the initial pH of CR solutions from 3 to 11 using 0.1N HCl or NaOH solutions, with the initial CR concentration fixed at 400 mg/l. The change in pH during adsorption was studied at acidic pH (pH 3 and 5), neutral pH (pH 7) and alkaline pH (pH 9 and 11), with the initial CR concentration at 400 mg/l. At the end of the adsorption period of 30 min, the supernatant solution was collected by centrifugation at 3000 rpm for 30 min. The amount of CR in the solutions before and after adsorption was analyzed at 570 nm using a DR5000 spectrophotometer (HACH, USA).

Effect of adsorbent dose:

The batch adsorption was carried out on a shaker at 150 rpm and 30°C using 100 ml ErlenmeyerFlask containing 0.5 g of adsorbent and 50 ml of CR solutions of desired concentration and pH. In this study, raw Neem leaf litter powder and carbon prepared from Neem leaf litter were used as adsorbents separately. All the adsorption experiments were conducted in triplicate. The effect of adsorbent dosage on CR (C₀ = 400 mg/l) adsorption was tested by varying the adsorbent dosage from 0.1g/50 mL to 05 g/50 mL.

Results and Discussion:

Effect of Contact Time:

The effect of contact time was studied to determine the time taken by adsorbent to reach equilibrium at pH 5 with the initial CR concentration fixed at 400

mg/l. The percentage dye removal increases with increase with contact time till equilibrium is reached. Equilibrium time is the time after which no significant adsorption place. The equilibrium time for Cr adsorption on both RNLL and NLLC was found to be 20 min (Figure 1)

Effect of Initial Dye Concentration:

Equilibrium isotherm studies were carried out with different initial concentrations of CR (100 – 500 mg/l) at 30°C and pH 5. The percentage dye removal decreases with increase in initial dye concentration for RNLL and it remains constant for NLLC. This means that adsorption capacity increases for RNLL and remains constant for NLLC. (Figure 2)

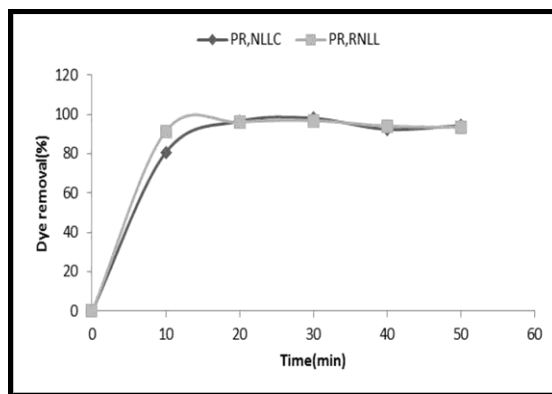


Figure 1. Effect of contact time on adsorption

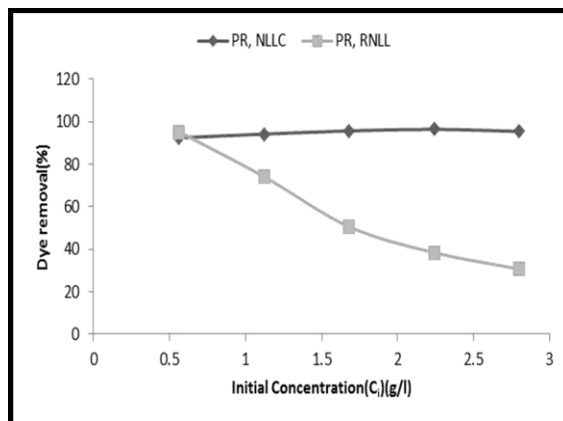


Figure 2. Effect of initial concentration on adsorption

Effect of pH:

The influence of pH on CR removal was studied by varying the initial pH of CR solutions from 3 to 11 using 0.1N HCl or NaOH solutions, with the initial CR concentration fixed at 400 mg/l. The change in pH during adsorption was studied at acidic pH (pH 3 and

5), neutral pH (pH 7) and alkaline pH (pH 9 and 11), with the initial CR concentration at 400 mg/l. The percentage dye removal decreases with increase in pH for RNLL and it remains constant for NLLC. From figure 3 it is evident that acidic region is favorable for NLLC and basic region is favorable for RNLL.

Effect of adsorbent dose:

The batch adsorption was carried out on a shaker at 150 rpm and 30°C using 100 ml Erlenmeyer flask containing 0.5 g of adsorbent and 50 ml of CR solutions of desired concentration and pH. The percentage dye removal increases with increase in adsorbent dosage for both RNLL and NLLC. (Figure 4)

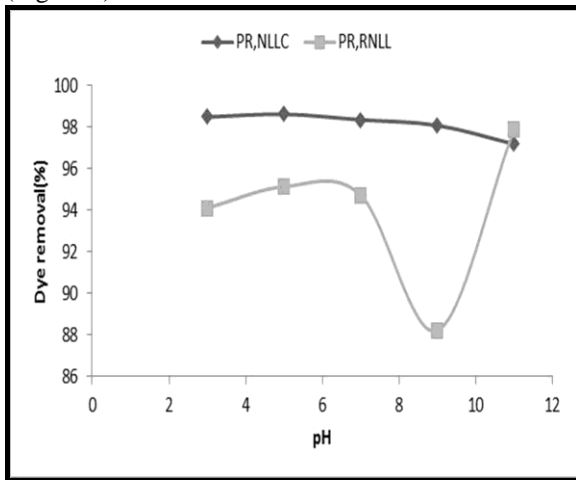


Figure 3. Effect of pH on dye adsorption

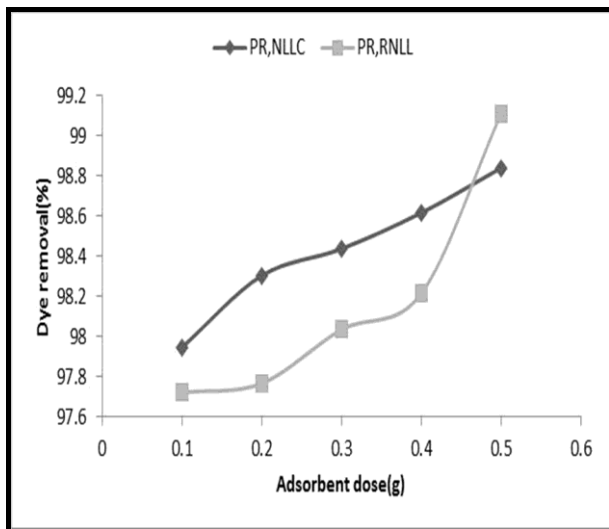


Figure 4. Effect of adsorbent dose on dye adsorption

Adsorption Isotherm:

The isotherm provides information on the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the operating conditions. Two adsorption isotherms, namely, Langmuir and Freundlich isotherms were tested in this present study. The Langmuir isotherm model showed a good fit with the equilibrium experimental data for both RNLL and NLLC. (Figures 5 to 8)

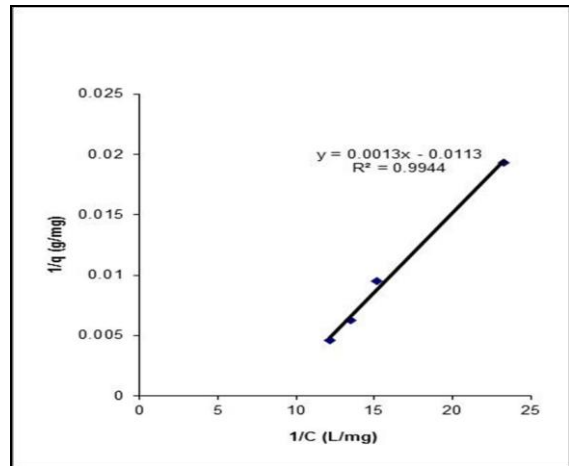


Figure 5. Langmuir Isotherm of CR adsorption on NLLC

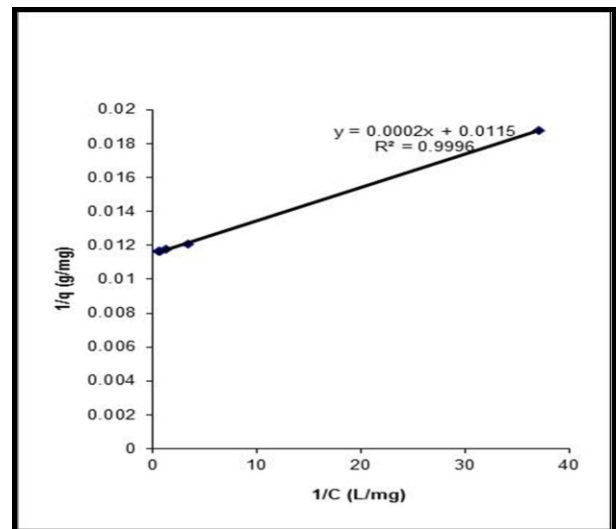


Figure 6. Langmuir Isotherm of CR adsorption on RNLL

Freundlich isotherm represents adsorption equilibrium and is widely used. The empirical equation is capable of describing the adsorption of organic and inorganic compounds on a wide variety

of adsorbents. Freundlich equation fits in nearly all experimental adsorption-desorption data and is especially useful for data from highly heterogenous sorbent systems.

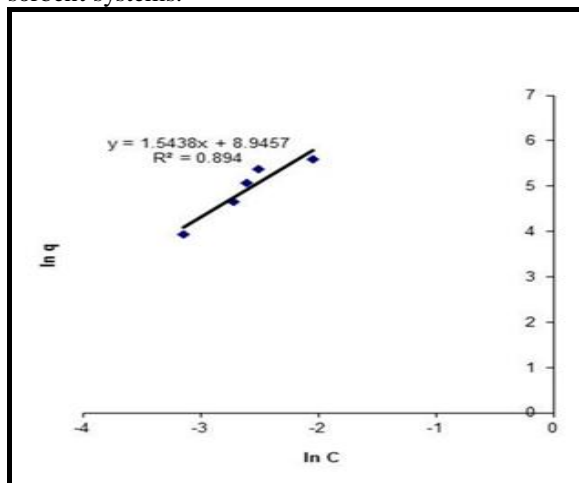


Figure 7. Freundlich Isotherm of CR adsorption on NLLC

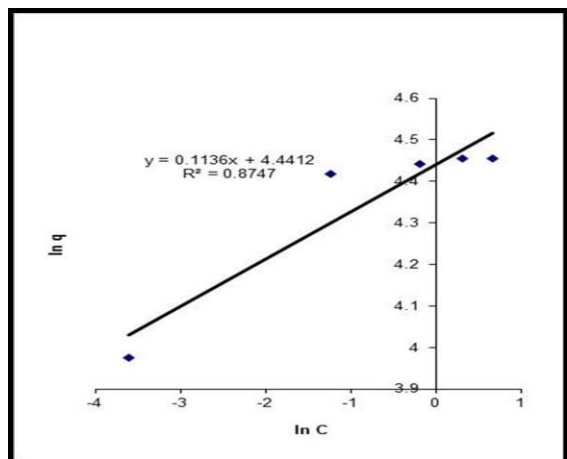


Figure 8. Freundlich Isotherm of CR adsorption on RNLL

Adsorption Kinetics:

Equilibrium study is important in determining the efficacy of adsorption. It is also necessary to identify the adsorption mechanism for a given system. Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction.

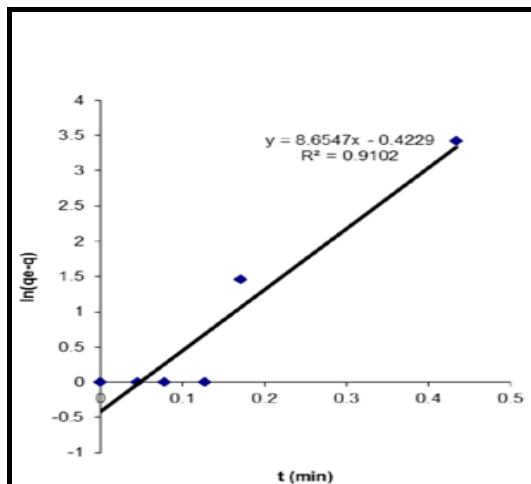


Figure 9. Pseudo First Order Kinetics for CR adsorption on NLLC

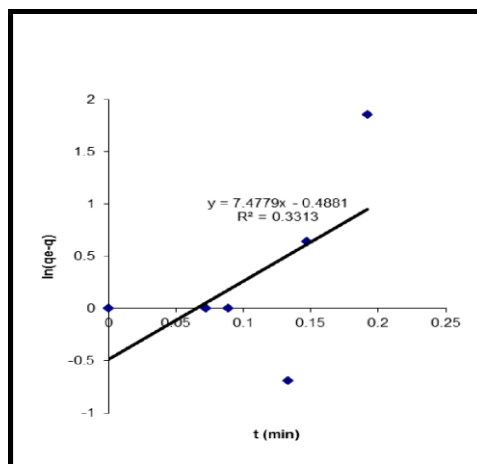


Figure 10. Pseudo First Order Kinetics for CR adsorption on RNLL

Adsorption kinetics is expressed as the dye removal rate that controls the residence time of the dye in the interface of adsorbent and solution. Pseudo first order and pseudo second order kinetic models were used for CR adsorption on RNLL and NLLC. The pseudo second order kinetic model showed a good fit with the equilibrium experimental data for both NLLC and RNLL. (Figures 9 to 12)

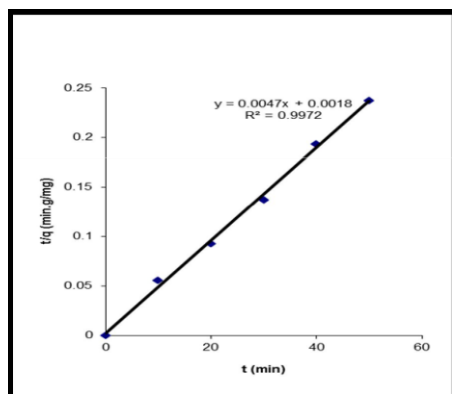


Figure 11. Pseudo second Order Kinetics for CR adsorption on NLLC

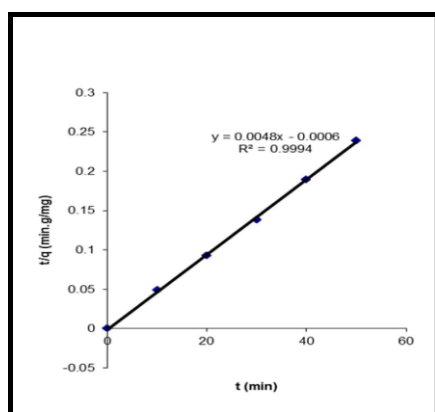


Figure 12. Pseudo Second Order Kinetics for CR adsorption on RNLL

Conclusion:

The adsorption of Congo red (CR) onto carbon prepared from Neem leaf litter was investigated. The Langmuir isotherm model showed a good fit with the equilibrium experimental data. The kinetic data showed better fit to the pseudo second-order rate model. The adsorption of Neem leaf litter showed the highest adsorption capacities of CR compared to any other adsorbents and would be a good method to increase adsorption efficiency for the removal of anionic dyes in a wastewater treatment process.

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