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Study of sorbent properties of powdered and chemically treated leaves of *Azadirachta indica*

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Abstract: **The leaves of *Azadirachta indica* (neem) have proven medicinal properties; in addition nowadays leaves of neem were also used for adsorption properties. In continuation with adsorption research, here, we report neem leaves as a bio-sorbent in the purification process of water effluent polluted by Acid Blue 15 dye. In dye removal process, appreciable uptake of it was observed by neem leaves using batch adsorption method. Further, thermodynamic and kinetic findings opened that adsorption was in alignment with Freundlich isotherm and pseudo first order respectively. Progress in the findings of other parameters like effect of pH, adsorbent dose and effect of contact time made the powdered and chemically treated neem leaves a viable selection for the removal of Acid Blue dye from the industrially polluted water.**

Index Terms: **Azadirachta Indica, Acid Blue 15, Langmuir, Neem, Pseudo first order Introduction**

I. INTRODUCTION

Synthetic dyes, comprising one or more chemically active functional groups in their molecular structure, are frequently applied on the surface of textiles owing to their wide scope of shades of color, ease of application and long lasting fastness properties. These dyes have been largely used by industries such as food, textile, cosmetic, pulp, leather, wood, pharmaceutical, paper, pigments to meet the manifold objectives (Chen et. al., 2011). Carcinogenicity, mutagenicity, toxicity, teratogenic and stability against biodegradation may be associated properties with the synthetic dyes (Chung et. al., 1981). These kinds of dye, if released in water, also may produce skin irritation and dermatitis in human. When untreated or improper discharge of highly colored effluent rich in dyes used by the above mentioned industries, directly into aquatic ecosystem regularly happens, it leads the balance of aquatic life to high level of discomfort (Talarposhti et. al., 2001). To minimize the concentration of dye in water effluents, numerous physical and/or chemical processes such as coagulation (Yang et. al., 2013), oxidation processes (Strickland and Perkins, 1995), membrane technologies (Wu et. al., 1998), microbial degradation (Thung et. al., 2018), adsorption (Ho and Mckay, 1998), flocculation (Vanderviere et. al., 1998), bioaccumulation (Aksu, 2003) and electrochemical methods (Clematis et. al., 2017) had been effectively employed in the past research. However, bio-sorption process has merits over other processes in terms of greener approach, lesser cost, ease of availability, regeneration and reusability (Kapdan and Kargi, 2002). Leaves being lingo-cellulosic in nature can be a choice as bio-adsorbent (Laura et. al., 2019). Peanut, hulls, fungi, bacteria, algae are some other biomasses used in the literature (Alves et. al. 1993). A leaf of Azadirachta Indica, commonly known as neem, is also utilized as bio-adsorbent (Sarma and Bhattacharya, 2001). Neem leaf powder is applied to remove the synthetic dyes from waste water loaded with dye like crystal violet (Khattri and Singh, 2000), malachite green (Ibrahim and Sani, 2014), blue BFG (Arafath et. al., 2013), methylene blue (Saengbutr et. al., 2014), congo red (Ibrahim and Sani, 2014), orange MERL (Arafath et. al., 2013) and metal ions (Gopalkrishnan, 2013).

The Acid Blue 15 (AB 15) dye a variant of triarylmethane class and acid dyes is preferably used as textile finisher to dye the threads of wool, mixed fabric, silk, leather and also printing purposes. Because of its bright blue hue, industries use it on commercial level for better visuals. Removal of the AB 15 is done by the investigators by harnessing adsorption processes with biomass as bio-adsorbent like chitosan (Mohammed and Wala, 2020), macroalga (Padmesh et. al., 2006; Mohammad, 2014), rice husk ash (Sumanjit Prasad, 2001), bagasse charcoal, kiln ash, cow dung charcoal, pea shells charcoal, used tea leaves charcoal, wheat straw charcoal (Kaur et. al., 2008), biofilms (Sharma et. al., 2004), red mud (Balarak et. al., 2015),sun flower seed hull (Thinakaran et. al., 2008) and pomelo skin (Foo and Hameed, 2011). Present research is performed to see the proficiency of Azadirachta Indica leaf powder in dealing with the treatment of simulated waste water with the dye AB 15.

II MATERIALS AND METHODS

A Preparation of Adsorbent

Matured Neem leaves picked up locally was washed from distilled water to make it free from dirt and any soluble impurities or microbes present on the surface of leaf. Leaves dried at 85°-90°C was powdered and sieving with mesh size < 15µm was performed to ensure the uniformity in size. Chemical activation was carried out by mixing sieved neem leaves powder (25 gm) and orthophosphoric acid (20 ml) at 100 rpm for 1hour at room temperature. Mixture was ignited in a silica crucible at 250°C for 25-30 minutes in furnace. Acidified neem leaves powder at room temperature was treated thoroughly with distilled water to make it free from extra acid. The dried leaf powder was stored into desiccators for further use.

B Acid Blue 15 dye solution

1000 ppm of AB 15 dye (C. I.42645) was prepared with hot water and subsequently cooled solution was filtered for removal of undissolved solids. This was used as stock solution for further studies.

C Methods

Chemically activated and carbonized leaves powder (120 mg) was shaken with 100 ppm of AB 15 dye solution (50 ml) for predetermined time duration. The resultant solution was filtered using Whatmann filter paper and absorbance of the filtrate solution was observed on UV-Visible spectrophotometer at λmax= 564 nm. For regeneration of adsorbent, desorption studies were carried out by stirring leaves powder uploaded with AB 15 dye for 100 minutes in water (50 ml) maintained at various pH.

D Structure of Adsorbate

Figure 1 depicts the structure of the dye.

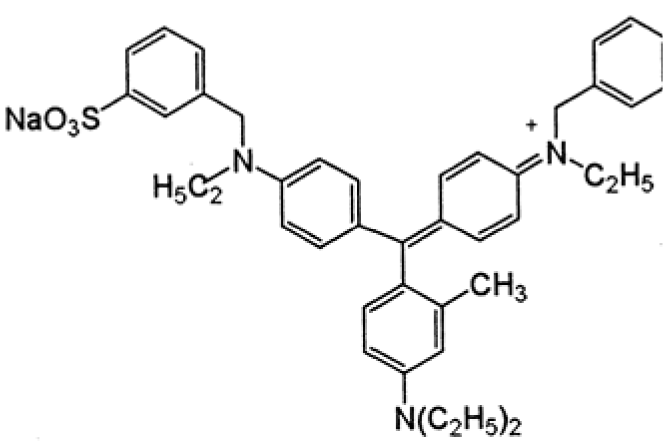

Figure 1

E Batch adsorption studies

The adsorption parameters were investigated by batch adsorption methods.

1 Adsorption Experiments

Sieved and powdered neem leaves (120 mg) had been employed to study the adsorption of acid blue 15 dye by Batch experiments.

2 Effect of Contact time

Neem leaves powder (120 mg) was mechanically stirred with 100 ppm of AB 15 (50 ml) at 180 rpm and natural pH was maintained throughout the study for the assumed time interval.

3 Effect of adsorbent dose

50 ml of 100 ppm Acid Blue 15 dye solution with different doses of powdered neem leaves (0.05 – 2.5 g) was stirred at 180 rpm at is natural pH for 80 minutes.

4 Effect of pH

It was investigated for the study of effect of pH on adsorption of AB 15 (50 ml of 100 ppm) on the surface of adsorbent (120 mg) at 180 rpm for 80 minutes within range of 2 – 12 which was attained by 0.1 M HCl or 0.1 M NaOH.

5 Desorption Study

This was evaluated by mixing 120 mg of powdered neem leaves with 50 ml of 100 ppm dye maintained at different pH ranges.

III Results and Discussion

A Effect of Contact Time

It is an important parameter in the sorption process and for its utility. The sorbent and dye was mechanically agitated at their natural pH and the study was performed at increment of 10 minutes for predetermined time period (0-110 minutes). Initially rate of sorption was high and gradually it decreased and reached to equilibrium after 80 minutes with maximum removal of 93% of dye from the solution. Probable reason for higher rate of sorption in the beginning may due to the access of high number of binding sites at the surface of sorbent for the dye molecules.

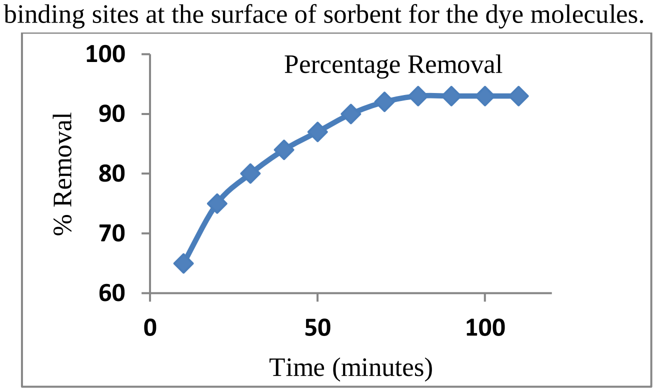

Figure 2

B Effect of adsorbent dose

Rate of adsorption increased sharply with initial doses of bio-sorbent, though gradually rate decreased and attained equilibrium with maximum adsorption up to 93 % by the 210 mg dose of bio-sorbent as depicted in figure 3. High rate of removal of dye may be due to increase in the surface area with increasing the dose of neem leaf powder.

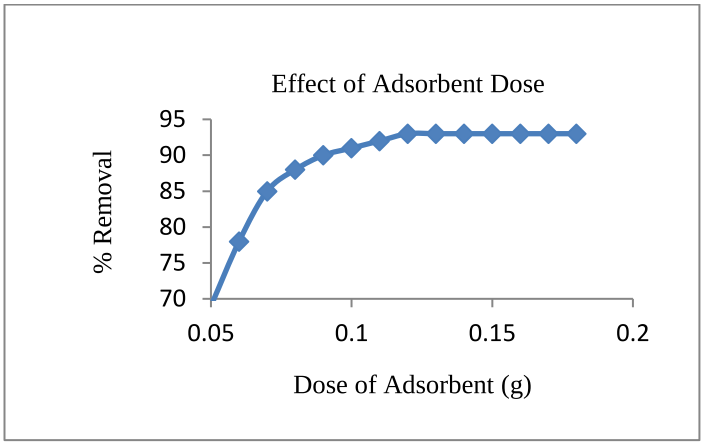

Figure 3

C Effect of pH

Figure 4 explains the effective removal of dye is observed in the pH range between 2 to 3. With lower pH, due to increased number of protons in the solution, the surface of sorbent becomes positively charged. Then, electrostatic force plays the role between positively charged surface and negatively charged dye molecules (Nourmoradi, 2014).

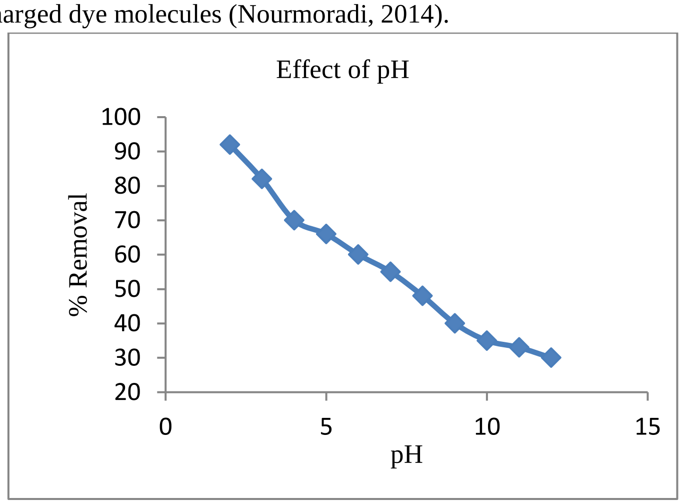

Figure 4

D Desorption Study

Desorption study (Figure 5) can be used to ensure about reusability and regeneration of sorbent. Study revealed that at higher pH, sorbent can be regenerated but some percentage of dye permanently affixed. It can be inferred that there may some kind chemical bond formation between dye molecules and molecules on the surface of adsorbent to some extent after adsorption process.

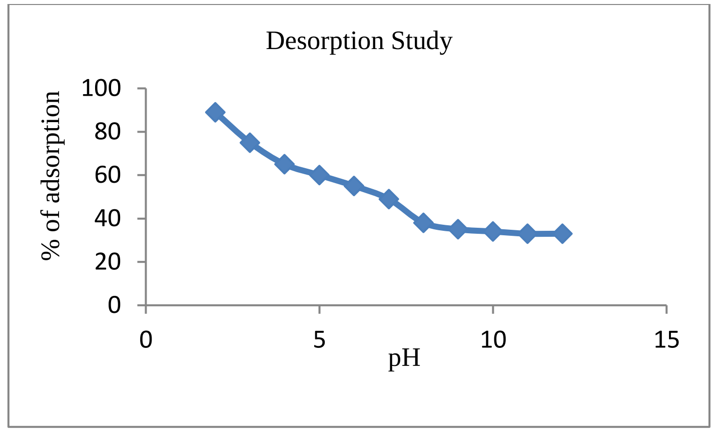

Figure 5

E Adsorption Isotherm

Equilibrium distribution was studied by using isotherm models. Among the various models, experimental findings at ambient temperature were indicative of Langmuir isotherm model (Vimonses et. al., 2010) as best fit model to explain the nature of equilibrium on interface of molecules between sorbent and AB15. Langmuir model in the linear form can be explained as

$$\frac{q_e}{C_e} = \frac{1}{q_{max}b} + \frac{1}{q_{max}} C_e$$

Where q_e is amount of dye at equilibrium in (mg/g), q_{max} is related to adsorption capacity and measured in (mg/g) i.e. maximum adsorption of dye per unit mass of sorbent, b is Langmuir constant and is measure of affinity of binding sites. Figure 6 describes the best fitting model the experimental data for the adsorption is Langmuir model with regression coefficient (R^2 = 0.996) and Langmuir constant (b = 0.0689).

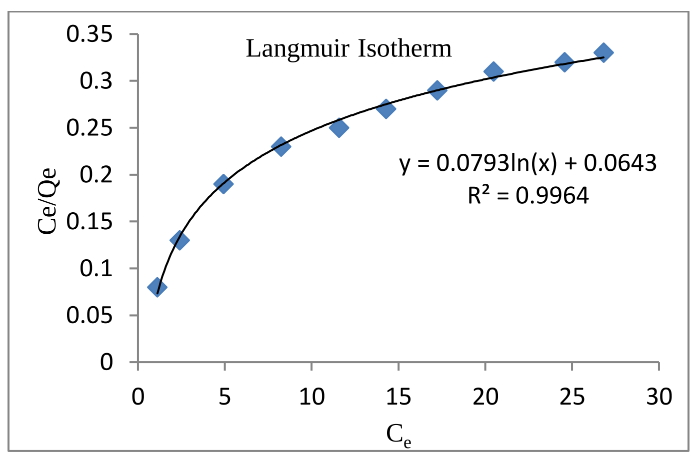

Figure 6

F Kinetics

Kinetic models are used to explore the mechanism of sorption and to estimate time of retention of dye sorbate on the surface of sorbent Kinetics helps in controlling the potential parameters and conditions optimum for full batch process. The investigation and study of graph for kinetic parameters related the data which were suitable for pseudo first order kinetics as the best fitting model. Langergen's equation (Langergren, 1898) was used to plot the observation for the sorption between AB 15 and powdered neem leaves. Equation employed is: $\log (Q_e - Q_t) = \log Q_e - \frac{K_{ad}}{2.303}t$ where Q_t is the amount of dye adsorbed (mg/g) at time *t*, Q_e is the amount of dye adsorbed at equilibrium, and K_{ad} is the adsorption constant of first-order sorption process (min^{-1}). Figure 7 depicts the kinetic nature of sorption and presumptive mechanism will follow the pseudo first order kinetic with high correlation value i.e. 0.995.

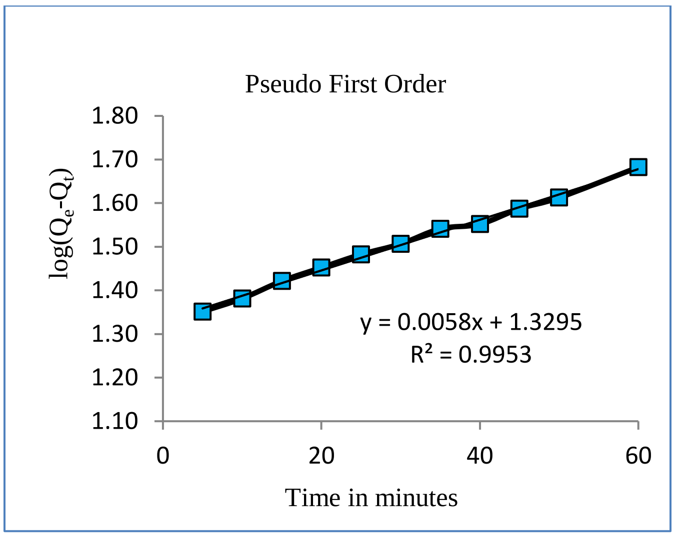

Figure 7

IV Conclusion

Use of chemically activated powdered leaves of Azadirachta Indica to grab the particles from water effluents was successful up to 93 %. Batch adsorption study at room temperature was performed to obtain the optimum operational parameters. However, the parameters may change when same will be followed for continuous or bed column method. In laboratories it followed the lower pH, pseudo first order kinetics and Langmuir equilibrium model. The nature of sorption can be predicted as monolayer and chemisorptions between AB 15 and Sorbent. Neem leaves in water after desorption process can impose secondary level of toxic effects like killing of micro-organisms.

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